EVALUATION OF EXCHANGE SELECTIVITIES
SUGGESTED FOR USE IN MODELS OF
CATION TRANSPORT THROUGH POROUS MEDIA

By

STEVEN ALEXANDER GRANT

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1987

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of a Dissertation Presented to the Graduate School
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EVALUATION OF EXCHANGE SELECTIVITIES SUGGESTED FOR USE IN
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DECEMBER, 1987

Chairman: Robert S. Mansell
Major Department: Soil Science

Batch cation exchange and column experiments were
conducted to evaluate several exchange selectivities which
have been suggested for describing cation exchange reactions
in solute transport models. The batch cation experiments
measured cation equilibria with an analytical grade
macroporous sulphonic polystyrene–divinylbenzene cation
resin. The resin was equilibrated with binary and ternary
solutions of $Ca(ClO_4)_2 \cdot 4H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, and $NaClO_4 \cdot H_2O$ at
constant ClO_4 concentrations. Adjusted Vanselow selectivity
coefficients were calculated for exchange equilibria with the
cation resin, as well as for exchange equilibria reported in
the literature with montmorillonite and with a Yolo loam
soil. Least squares regression of the natural logarithm of
the adjusted Vanselow selectivity coefficients on the

exchanger phase cation equivalent fraction were calculated for both the binary and ternary systems.

The batch exchange and column experimental data were used to evaluate mole fraction, equivalent fraction, and statistical thermodynamic exchanger phase reference functions. The predictive utilities of regressions of the adjusted Vanselow selectivity coefficient on exchanger phase composition were evaluated. Four tests were used to evaluate these reference functions and regression equations: 1) their closeness to calculated exchanger phase activities; 2) accuracy of estimates of exchanger phase composition based on their use; 3) accuracy of the predicted cation concentration distributions with cumulative column effluent volume; and 4) accuracy of the predicted first moment of the cation distribution with cumulative effluent volume. The mole fraction was closest to the calculated exchanger phase activity for both synthetic resin and montmorillonite exchangers. With a montmorillonite system, the mole fraction was the most reliable estimator of exchanger phase composition, while the equivalent fraction was the most reliable for the resin exchanger. With the resin exchanger, the statistical thermodynamic reference function gave the most reliable estimate of column effluent cation concentration. In a column packed with the Yolo loam soil, the mole fraction gave the most accurate prediction of column response. Use of variable Vanselow selectivity coefficients gave more accurate predictions in both the batch

and column experiments. Compared to the use of binary data, the use of ternary data improved predictions of batch exchange equilibria but not predictions of column response.

INTRODUCTION

Many of the solutes which move through natural and
artificial porous media are cations. Consequently, cation
movement in soils and porous media is worthy of study. The
movement of cations in soils can affect soil fertility, soil
salinity, soil sodicity and the leaching of some pesticides.
The movement of cations in porous media generally determines
the cation movement from brackish water injected into deep
aquifers, the response of ion chromatography columns, and the
performance of ion exchangers used to deionize saline and
municipal waters.

Cation movement in soils and other porous media is
governed by both physical and chemical processes. The major
physical process is the mass flow of the solution through
porous media which is in turn governed by the nature of the
porous media, the amount of other fluids (e.g. air, and, less
commonly, water-immiscible hydrocarbons) present and the
potential energy gradients within the water which determine
the rate and direction of the fluid flow.

The movement of cations through soil is also affected by the
chemical interactions between solute in solution and the
solids in the soil matrix. Since most soil and aquifer

1

minerals have net negative electrostatic charge due to isomorphic substitution in the mineral crystal, ion exchange is an important cation sorption mechanism. In an exchange reaction, ions in solution sorb on the exchanger surface to satisfy the electrostatic charge of the exchanger. Ions adsorbed by ion exchange can be displaced by a counterions able to satisfy the same amount of electrostatic charge in the exchanger. Accordingly, ion exchange reactions are distinguished by their stoichiometry and reversibility (Helfferich, 1962). Cations may be removed from or added to the soil solution by mechanisms other than ion exchange. For example, the cation may complex with organic ligands or sites on the surfaces of soil minerals. Another mechanism which may control the soil solution cation concentrations is the combined solubilities of the minerals present in the soil matrix. For example, if present, calcium carbonate ($CaCO_3$) and other calcic minerals will control, to a large extent, the soil solution concentration of calcium (Ca^{2+}). Another mechanism affecting soil monovalent cations in solution such as potassium (K^{1+}) and ammonium (NH_4^{1+}) is their formation of inner-sphere complexes between the layers of micaceous clays, again, if found, in the soil matrix. Once such complexes are formed, these cations can be released slowly into the soil solution.

LITERATURE REVIEW

Mathematical Formulation of Cation Transport

General partial differential equations which describe the one-dimensional convective-dispersive (sometimes referred to as advective-dispersive) transport of each cationic solute species i through porous media under transient water flow conditions may be written in the form

$$\frac{\delta}{\delta z}\left(\theta D \frac{\delta c_i^s{}'}{\delta z} - \theta u c_i^s{}'\right) - \frac{\delta}{\delta t}(\theta c_i^s{}' + \rho_b m_i^e{}') =$$

$$L_s^1 \theta c_i^s{}' + L_e^1 \rho_b m_i^e{}' - L_s^0 \theta - L_e^0 \rho_b \qquad [1]$$

where

z = length in the z direction (dm),

θ = volumetric water content (dm^3 dm^{-3}),

D = dispersion coefficient (dm^2 s^{-1}),

u = interstitial velocity (dm s^{-1}),

$c_i^s{}'$ = ion i solution equivalent concentration ($\frac{1}{z_i}$mol dm^{-3}),

3

ρ_b = porous medium bulk density (kg dm^{-3}),

$m_{i,}^e$ = ion i solid solution equivalent molality ($\frac{1}{z_i}$ mol kg^{-1}),

t = time (s),

L_s^1 = first-order rate coefficient of decay in solution (s^{-1}),

L_e^1 = first-order rate coefficient of decay in solid (s^{-1}),

L_s^0 = zero-order rate coefficient of production in solution (mol dm^{-3} s^{-1}), and

L_e^0 = zero-order rate coefficient of production in solid (s^{-1})

(van Genuchten and Alves, 1982).

Since chemical processes such as those described in the opening paragraphs of the introduction may confound one another in both batch and column experiments, this study will restrict itself to the effects of the ion exchange reaction upon the flux of cations with a solution flowing through porous media. To make the examination of the effects of ion exchange on cation transport through porous media, the above equation can be simplified by restricting the system both chemically and physically. Simplification of the equation must be accompanied by concomitant restrictions in the nature of the porous media, the chemical make-up of the solution which flows through it, and the physical nature of the solution flow through the porous medium. First, the

volumetric water content and the dispersion coefficient are held constant. Second, the chemical solute-solid interactions are limited to ion exchange. Third, it is assumed that the ion exchange reactions are instantaneous locally. Ion exchange is a kinetic process, but the rate-determining step of the process is not the reaction at the exchanger surface, but the diffusion of the counter-ions to and from the exchanger surface (Helfferich, 1962). The kinetics of the ion exchange process will be determined by the diffusive distance and the resistance to mass flow the ion experiences as it moves to and from the exchanger surface. Accordingly, it is the structure, rather than the surface chemistry, of the porous media which determines effective rate of the exchange reaction. For porous media with sufficiently high molecular diffusion coefficients and sufficiently low dispersion coefficients, the ion exchange reaction may be assumed to be occurring instantaneously in solute transport models (James and Rubin, 1979).

If the three restrictions described in the preceding paragraph are applied the following general form of partial differential equation applies for each cationic solute i

$$\frac{\delta c_i^s}{\delta t} + \frac{\rho_b}{\theta} \frac{\delta m_i^e}{\delta t} = D \frac{\delta^2 c_i^s}{\delta t^2} - u \frac{\delta c_i^s}{\delta z}. \qquad [2]$$

The simultaneous solution of three of these partial differential equations, one each for three heterovalent

cations flowing through exchanging porous media, will occupy the balance of this study.

Thermodynamic Description of Ion Exchange

By neglecting kinetic effects, the ion exchange phenomena may be described by equilibrium thermodynamics. Before beginning with this description, some terms should be defined. The <u>exchanger-solution system</u> is composed of the water, the solid ion exchanger, which is assumed here to convey only a constant negative electronic charge, and the salts, which are assumed here to be completely disassociated. While the components are commingled, the exchanger-solution system can be viewed as being composed of two distinct phases, designated the exchanger phase and the solution phase. The <u>exchanger phase</u> consists of the solid ion exchanger and all cationic solutes sorbed to the solid ion exchanger as well as water molecules of hydration for the cations and the solid exchanger. The <u>solution phase</u> consists of everything, aside from the gases above the mixture, which is not ascribed to the exchanger phase (i.e. the water, the anionic solutes, and the remainder of the cationic solutes).

A binary cation exchange reaction (one which involves two cationic solutes) may be expressed by

$$z_j \, \mathbf{i} \mathbf{a}^s_{z_i} + z_i \, \mathbf{j} \mathbf{x}^e_{z_j} \; \overset{\rightarrow}{\leftarrow} \; z_j \, \mathbf{i} \mathbf{x}^e_{z_i} + z_i \, \mathbf{j} \mathbf{a}^s_{z_j} \qquad [3]$$
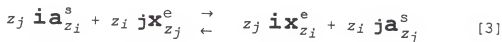
where the two cations i and j, having valences z_i and z_j, respectively, are both assumed to be found in the solution completely disassociated from the anion a and in the exchanger phase sorbed to the exchanger x. The cationic solutes in the exchanger phase are indicated with a superscript "e" to differentiate them from non-exchangeable molecules of the same cation which may be constituents of the cation exchanger.

The <u>thermodynamic exchange constant</u> for this reaction relates the activities of cations in the exchanger and solution phases:

$$K_{exi/j} = \left(\frac{a_i^e}{a_i^s}\right)^{z_j} \left(\frac{a_j^s}{a_j^e}\right)^{z_i} \qquad [4]$$

where

$\quad K_{exi/j}$ = thermodynamic exchange constant,

$\quad a_i^e$ = activity of solute i in the exchanger phase,

and

$\quad a_i^s$ = activity of solute i in the solution phase.

<u>Solution Phase and Exchanger Phase Reference Functions</u>

While the activities of electrolytes in solution are measurable, solution phase and exchanger phase activities of individual cationic solutes are not measurable directly. Therefore, experimentally measurable activity estimates are

used in the application of thermodynamic theory to ion-exchange reactions in soils. A <u>reference function</u> is a function of experimentally measurable quantities which approximates thermodynamic activities (Wall, 1974). A reference function must approach smoothly the activity as the system approaches its reference state. This criterion is represented symbolically by

$$\lim_{\zeta \to \zeta^*} \frac{a_i}{r(\zeta)} = 1$$

where

a_i = activity of i,

$r(\zeta)$ = a reference function, and

ζ^* = the reference state.

Both solution concentration and solution molality may be used as reference functions of solution phase solute activity. Solution concentration is the appropriate reference function of the solute in the solution phase for models of ion exchange with transport in porous media when water content is expressed as a volumetric ratio. The American Society of Agronomy (1984) has designated the mass ratio as the preferred unit to express soil water content. If the mass ratio is adopted to express soil water content, then solution molality would be a more tractable selection as the reference function for solution phase activity of the solutes.

Several exchanger phase reference functions have been proposed for thermodynamic models of ion exchange. For

purposes of this discussion, all exchanger phase reference functions can be expressed symbolically by

$$r_i^e = \frac{n_i^e}{D_i}$$

[5]

where

r_i^e = exchanger phase cation i reference function,

n_i^e = number of cation i in the exchanger phase (mol),

and,

D_i = a denominator, exact form depends on particular exchanger phase reference function.

In 1932, Vanselow proposed the exchanger phase mole fraction as an estimate of the exchanger phase activity. If the exchanger phase activity is equal to the exchanger phase mole fraction (that is, the exchanger phase activity coefficient, f_i, is unity), the exchanger phase behaves as an ideal solid solution obeying Raoult's law. Sposito and Mattigod (1979) have noted that trace metal-Na exchange on Camp Berteau montmorillonite behave as an ideal solid solution. It is not clear if the exchanger phase of soils and soil minerals behave consistently as ideal solid solutions. Krishnamoorthy and Overstreet (1948), however, have argued that the application of Raoult's law to ion-exchange equilibria ignores the spatial arrangement of charge sites on the exchanger surface. If the mole fraction is accepted as the exchanger phase reference function, the denominator, D_i, is

$$D_i = \sum_{k=1}^{n} n_k^e \qquad\qquad [6]$$

where

n = number of cations in the exchange system.

Using techniques of statistical thermodynamics, Krishnamoorthy et al. (1948) adopted the gas adsorption theory of Guggenheim to cation exchange reactions. They contended that the mole fraction reference function failed to take into account the spatial distribution of surface functional groups on the exchanger surface. This shortcoming could be remedied by viewing the exchanger surface as a two-dimensional array, each surface functional group having four nearest neighbors. Krishnamoorthy and Overstreet (1949) wrote that this reference function would be an appropriate model for cations adsorbed to "clays and synthetic resins." The result of this approach suggested a more complicated estimate of exchanger phase activity with a denominator appropriate for their estimate as

$$D_i = \frac{1}{y_i} \sum_{k=1}^{n} y_k \, n_k^e \quad \text{where } y_i = \frac{z_i + 1}{2} \; . \qquad [7]$$

Gaines and Thomas (1953) suggested the equivalent fraction as an estimate of exchanger phase activity. The denominator corresponding to this reference function is

$$D_i = \frac{1}{z_i} \sum_{k=1}^{n} z_k \, n_k^e \, .$$ [8]

While the present study ignores reactions other than ion exchange, there are several computer programs in the published literature which attempt to calculate the complex chemical equilibria in soil solutions. The most sophisticated of these, GEOCHEM, is an adaptation of REDEQL2 for soil solutions (Sposito and Mattigod, 1980; Morel and Morgan, 1972). While no explicit exchanger phase reference function is presented, the reference function used implicitly by GEOCHEM is the "concentration" of cation-exchanger complex in solution in moles cation-exchanger complex per cubic decimeter of solution.

Exchange Selectivity Coefficients

The exchanger phase and solution phase reference functions reviewed above may be combined to yield selectivity coefficients. For the purposes of this study, the defining relation is the equation which defines the thermodynamic exchange constant in terms of the exchanger phase and solution phase reference functions

$$K_{exi/j} = \left(\frac{f_i \, r_i^e}{\gamma_i \, r_i^s}\right)^{z_j} \left(\frac{\gamma_j \, r_j^s}{f_j \, r_j^e}\right)^{z_i}$$ [9]

where

$K_{exi/j}$ = thermodynamic exchange constant,

r_i^e = cationic solute i exchanger phase reference function,

r_i^s = cationic solute i solution phase reference function,

f_i = exchanger phase activity coefficient, and

γ_i = solution phase activity coefficient.

The units of the reference function and the activity coefficient vary according to the reference function selected. Since activity is unitless, since

$$a_i^e = f_i r_i^e \text{ , and}$$

$$a_i^e = \gamma_i r_i^s \text{ ,}$$

the units of the activity coefficient are the inverse of those for the reference function for which it is defined.

The ion exchange selectivity coefficient, $k_{i/j}$, describing the exchange reaction equilibrium between ion i and ion j is defined as

$$k_{i/j} = \left(\frac{r_i^e}{r_i^s}\right)^{z_j} \left(\frac{r_j^s}{r_j^e}\right)^{z_i} \text{ .} \qquad [10]$$

The most recent recommendation by the International Union of Pure and Applied Chemistry (IUPAC) is that the term selectivity coefficient be used when the solutes in both phases were expressed in terms of concentrations (Irving, 1972). Since the choice of the concentration scale was left

up to the investigator by IUPAC, the most consistent usage
for this discussion is to use the selected reference function
as the appropriate concentration scale. The <u>adjusted
selectivity coefficient</u>, $k_{i/j}^a$, refers to the selectivity

coefficient in which the solution phase reference functions
are replaced by their activities

$$k_{i/j}^a = \left(\frac{r_i^e}{a_i^s}\right)^{z_j} \left(\frac{a_j^s}{r_j^e}\right)^{z_i}. \qquad [11]$$

Most of the commonly referenced selectivity
coefficients, the Vanselow selectivity coefficient, the
Gaines-Thomas selectivity coefficient and others are defined
with the cations in the solution phase represented by their
activities rather than a reference function. To be consistent
with the recommendations of IUPAC, these coefficients will be
referred to as adjusted selectivity coefficients. That is,
the common usage of the selectivity coefficient suggested by
Vanselow is represented by

$$k_{(V)\,i/j}^a = \left(\frac{x_i^e}{a_i^s}\right)^{z_j} \left(\frac{a_j^s}{x_j^e}\right)^{z_i} \qquad [12]$$

where

x_i^e = exchanger phase mole fraction.

In this study, this will be referred to as the "adjusted Vanselow selectivity coefficient" ($k^a_{(V)i/j}$) to be consistent with the IUPAC recommendation, even though this selectivity is not different from what is commonly understood to be the Vanselow selectivity coefficient. Accordingly, the term "Vanselow selectivity coefficient" ($k_{(V)i/j}$) is taken to be

$$k_{(V)i/j} = \left(\frac{x_i^e}{c_i^s}\right)^{z_j} \left(\frac{c_j^s}{x_j^e}\right)^{z_i} \qquad [13]$$

The thermodynamic exchange constant is related to the selectivity coefficient by

$$K_{exi/j} = \frac{\gamma_j^{z_i} f_i^{z_j}}{\gamma_i^{z_j} f_j^{z_i}} k_{i/j} \qquad [14]$$

and to the adjusted selectivity coefficient by

$$K_{exi/j} = \frac{f_i^{z_j}}{f_j^{z_i}} k^a_{i/j} \ . \qquad [15]$$

Other adjusted selectivity coefficients to be considered here include that suggested by Gaines and Thomas (1953), $k^a_{(GT)i/j}$, and the adjusted statistical thermodynamic proposed by Krishnamoorthy et al.(1948), $k^a_{(ST)i/j}$. These adjusted selectivity coefficients are, respectively,

$$k^a_{(GT)i/j} = \left(\frac{x_{i'}^e}{a_i^s}\right)^{z_j} \left(\frac{a_j^s}{x_{j'}^e}\right)^{z_i} \qquad [16]$$

and

$$k^a_{(ST)i/j} = \left(\frac{y_i\, m^e_i}{a^s_i}\right)^{z_j} \left(\frac{a^s_j}{y_j\, m^e_j}\right)^{z_i} \left(\sum_{k=1}^{n} y_k\, m^e_k\right)^{z_i - z_j} \quad [17]$$

where

x^e_{i} = cationic solute i exchanger phase equivalent

fraction, and

$$y_i = \frac{z_i + 1}{2}.$$

All of the preceding selectivity coefficients come from the chemistry of ion exchange. Other selectivity coefficients, to be considered later, have been suggested by their inclusion in various solute transport models.

Calculation of the Thermodynamic Exchange Constant and Exchanger Phase Activity Coefficients

The adjusted Vanselow selectivity coefficients determined from binary exchange experiments may be used to calculate the exchanger phase activity coefficients and the thermodynamic exchange constant (Argersinger et al., 1950; Sposito, 1981a). The thermodynamic exchange constant is related to the adjusted Vanselow selectivity coefficient by

$$K_{ex\,i/j} = \frac{f_i^{\,z_j}}{f_j^{\,z_i}}\, k^a_{(V)\,i/j} \quad\quad [18]$$

which by taking the natural logarithm of both sides yields

$$\ln K_{exi/j} = \ln k^a_{(v)i/j} + z_j \ln f_i - z_i \ln f_j. \qquad [19]$$

At equilibrium, changes in chemical potential of two cations and water in the exchanger phase are related by the appropriate form of the Gibbs-Duhem equation

$$n^e_i \, d\mu^e_i + n^e_j \, d\mu^e_j + n^e_w \, d\mu^e_w = 0 \qquad [20]$$

where

n^e_i = number of moles of cation i in the exchanger phase,

n^e_j = number of moles of j in the exchanger phase,

n^e_w = number of moles of solvent in the exchanger phase,

μ^e_i = exchanger phase cation i chemical potential,

μ^e_j = exchanger phase cation j chemical potential, and

μ^e_w = exchanger phase solvent chemical potential.

While it is not essential to the validity of the resulting equations, it will be assumed here that $d\mu^e_w = 0$. By using the definition of the chemical potential of the two cations in the exchanger phase

$$\mu_i^e = \mu_i^{eo} + RT \ln x_i^e f_i, \text{ and} \tag{21}$$

$$\mu_j^e = \mu_j^{eo} + RT \ln x_j^e f_j,$$

where

μ_i^{eo} = standard state exchanger phase cation i chemical potential, and

μ_j^{eo} = standard state exchanger phase cation j chemical potential.

The standard state for this discussion will be homoionic exchanger in contact with a solution having the same anion concentration as the equilibrating solutions and only cation i or j. By using the fact that,

$$dx_i = -dx_j$$

the following equation may be derived:

$$x_i \cdot d\ln f_i + x_j \cdot d\ln f_j = 0 \tag{22}$$

By using the derivative of the relation

$$\ln K_{ex\,i/j} = \ln k_{(v)\,i/j}^a + z_j \ln f_i - z_i \ln f_j$$

which is

$$d(\ln k_{(v)\,i/j}^a) = z_i \, d(\ln f_j) - z_j \, d(\ln f_i), \tag{23}$$

the differential equations

$$z_j \, d\ln f_i = (1 - x_i^e) x_i^e \cdot d\ln k_{(v)\,i/j}^a, \text{ and} \tag{24}$$

$$z_i \mathrm{dln} f_j = x^e_{j'} \, \mathrm{dln} k^a_{(V)i/j} \qquad [25]$$

where

$x^e_{i'}$ = exchanger phase cation i equivalent fraction, and

$x^e_{j'}$ = exchanger phase cation j equivalent fraction

may be derived. These equations may be integrated to yield

$$\ln f_i = \frac{1}{z_j} \left((x^e_{i'} - 1) \ln k^a_{(V)i/j} + \int_{x^e_{i'}}^{1} \ln k^a_{(V)i/j} \, dx^e_{i'} \right), \qquad [26]$$

and,

$$\ln f_j = \frac{1}{z_i} \left(x^e_{i'} \ln k^a_{(V)i/j} - \int_{0}^{x^e_{i'}} \ln k^a_{(V)i/j} \, dx^e_{i'} \right) \qquad [27]$$

Recalling that

$$\ln K_{exi/j} = \ln k^a_{(V)i/j} + z_j \ln f_i - z_i \ln f_j$$

these equations may be combined to provide an estimate of the thermodynamic exchange constant

$$\ln K_{exi/j} = \int_{0}^{1} \ln k^a_{(V)i/j} \, dx^e_{i'} . \qquad [28]$$

The standard free energy (ΔG°) of the exchange reaction may be calculated from the exchange constant by the use of the relation:

$$\Delta G^\circ = -RT \ln K_{exi/j} ,$$

where

R　　=　　Molar gas constant (J K^{-1} mol^{-1}),

T　　=　　Temperature (K),

(Lewis and Randall, 1961). This approach has been validated
for the calculation of the thermodynamic exchange constant
for soils (See, for example, Jensen and Babcock, 1973).

The Cation Transport Model of Rubin and James

The first numerical model of multispecies cation
transport through porous media to gain wide acceptance was
that of Rubin and James (1971). This seminal article is both
a good example of integrating complex chemical submodels in
solute transport models and an example of choosing the form
over the substance in the selection of a chemical submodel.
Recalling the convective-dispersive (or
advective-dispersive) equation [2] from the introduction

$$\frac{\delta c_i^s{'}}{\delta t} + \frac{\rho_b}{\theta} \frac{\delta m_i^e{'}}{\delta t} = D \frac{\delta^2 c_i^s{'}}{\delta t^2} - u \frac{\delta c_i^s{'}}{\delta z}$$

which may be written as

$$\frac{\delta c_i^s{'}}{\delta t} + \frac{\rho_b}{\theta} \frac{\delta m_i^e{'}}{\delta t} = L\, c_i^s{'} \qquad\qquad [29]$$

where the operator L is equal to

$$L = D \frac{\delta^2}{\delta t^2} - u \frac{\delta}{\delta z} .$$

Rubin and James defined their exchange selectivity coefficient as

$$k_{(RJ)i/j} = \left(\frac{m_{i'}^e}{c_{i'}^s} \right)^{z_j} \left(\frac{c_{j'}^s}{m_{j'}^e} \right)^{z_i} . \qquad [30]$$

Although Rubin and James state that this exchange selectivity coefficient need not be considered a constant, efforts to include variable selectivities in models following their development have not proven altogether successful for selected data. Most authors (e.g. Valocchi et al., 1981b) who have followed development by Rubin and James have assumed constant exchange selectivity.

In their development, Rubin and James made two assumptions. First, they, as do most authors, assumed that the cation exchange capacity (C) of the porous medium and the selectivity coefficients ($k_{(RJ)i/j}$) for each pair of cation species are constants.

$$\sum_{i=1}^{N} m_{i'}^e = C$$

They define the function, u_{ij}, a multispecies exchange isotherm as

$$u_{ij} = K_{(RJ)ij} \, c_{i'}^{s\,z_j} \, m_{j'}^{e\,z_i} - m_{i'}^{e\,z_j} \, c_{j'}^{s\,z_i} \qquad [31]$$

which after partial differentiation with respect to time, t, and division by $\dfrac{\delta u_{ij}}{\delta m_{j'}^{e}}$ yields

$$\frac{\dfrac{\partial u_{ij}}{\partial c_{i'}^{s}}}{\dfrac{\partial u_{ij}}{\partial m_{j'}^{e}}} \quad \frac{\partial c_{i'}^{s}}{\partial t} \quad + \quad \frac{\dfrac{\partial u_{ij}}{\partial m_{i'}^{e}}}{\dfrac{\partial u_{ij}}{\partial m_{j'}^{e}}} \quad \frac{\partial m_{i'}^{e}}{\partial t}$$

$$+ \quad \frac{\dfrac{\partial u_{ij}}{\partial c_{j'}^{s}}}{\dfrac{\partial u_{ij}}{\partial m_{j'}^{e}}} \quad \frac{\partial c_{j'}^{s}}{\partial t} \quad + \quad \frac{\partial n_{j'}^{e}}{\partial t} \quad = \quad 0$$

[32]

noting that

$$\sum_{j=1}^{N} \frac{\partial m_{j'}^{e}}{\partial t} \quad = \quad 0$$

and that

$$\sum_{j \ne i} \frac{\partial m_{j'}^{e}}{\partial t} \quad = \quad - \quad \frac{\partial m_{i'}^{e}}{\partial t} \quad ,$$

and summing the partial different equation above for all j=1,n gives

$$\frac{\partial m_i^{e'}}{\partial t} = \frac{1}{y_i} \left(v_{ii} \frac{\partial c_i^{s'}}{\partial t} - \sum_{j \neq i} \frac{\partial c_j^{s'}}{\partial t} \right)$$

[33]

where

$$y_i = 1 - \sum_{j \neq i} \frac{\dfrac{\partial u_{ij}}{\partial m_i^{e'}}}{\dfrac{\partial u_{ij}}{\partial m_j^{e'}}},$$

$$v_{ii} = \sum_{j \neq i} \frac{\dfrac{\partial u_{ij}}{\partial c_i^{s'}}}{\dfrac{\partial u_{ij}}{\partial m_j^{e'}}},$$

and

$$v_{ij} = - \frac{\dfrac{\partial u_{ij}}{\partial c_i^{s'}}}{\dfrac{\partial u_{ij}}{\partial m_j^{e'}}}$$

which, when substituted into the equation [29], gives the relation

$$\left(\theta \, y_i - \rho \, v_{ii} \right) \frac{\partial c_i^{s'}}{\partial t} - \rho \sum_{j \neq i} v_{ij} \frac{\partial c_i^{s'}}{\partial t} = L \, c_i^s,$$

[34]

This equation is then solved numerically, under the appropriate boundary and initial conditions, to give changes in cation solution concentration with time.

Crank-Nicholson Method

For the one-dimensional flow régime, equation [34] is a parabolic partial differential equation which may be solved numerically with a finite difference method, that is the Crank-Nicholson. Finite difference methods are relaxation methods, which means that the errors, or residuals, resulting for an initial approximation are considered as constraints that are to be relaxed (Hornbeck, 1975). New approximations are chosen to reduce the worst of the residuals until finally all are within a tolerance limit. The finite difference methods are based on the Taylor series expansion where the value of the function u at the point $j + \Delta x$ is approximated by

$$u(j + \Delta x) = u(j) + \Delta x \, u'(j) + \frac{\Delta x^2}{2!} u''(j) + \ldots$$

(James and James, 1976).

The first derivative of the function u with respect to x is therefore

$$u'(j) = \frac{u(j + \Delta x) - u(j)}{\Delta x} - \frac{\Delta x}{2!} u''(j) + \ldots$$

which may be expressed as

$$u'(j) = \frac{u(j + \Delta x) - u(j)}{\Delta x} - \frac{R_2}{\Delta x}$$

where

R_2 = is the remainder after 2 terms in the Taylor series.

Similarly, the second derivative may be estimated by

$$u''(j) = \frac{u(j + \Delta x) - 2u(j) + u(j - \Delta x)}{\Delta x^2} - \frac{R_3}{\Delta x^2}$$

There are several possible finite difference solutions of parabolic partial differential equations; the Crank-Nicholson is frequently used because the estimate is second-order accurate.

For example, the numerical approximation of the parabolic partial differential equation

$$\alpha \frac{\partial^2 f}{\partial x^2} = \frac{\partial f}{\partial y}$$

[35]

would be expressed in terms of the values of the five nearest neighbors of the node of interest. The parabolic equation [35] would be approximated by the equation

$$\frac{\alpha}{2}\left[\frac{f(j+\Delta x,k+\Delta y)-2f(j+\Delta x,k)+f(j+\Delta x,k-\Delta y)}{(\Delta x)^2}\right.$$

$$\left.+\frac{f(j,k+\Delta y)-2f(j,k)+f(j,k-\Delta y)}{(\Delta x)^2}\right]$$

$$=\frac{f(j+\Delta x,k)-f(j,k)}{(\Delta y)^2}$$

This equation for the x-y region of interest can be expressed in matrix form. The resulting matrix, in turn, can be solved in a straightforward manner using matrix multiplication.

$$
\begin{array}{cccccccc}
\gamma & 1 & & & & & \\
1 & \gamma & 1 & & & & \\
& 1 & \gamma & 1 & & & \\
& & - & - & - & & \\
& & & - & - & - & \\
& & & & 1 & \gamma & 1 \\
& & & & & 1 & \gamma
\end{array}
\qquad
\begin{array}{c}
f_{j+1,1} \\
f_{j+1,2} \\
f_{j+1,3} \\
- \\
- \\
f_{j+1,n+1} \\
f_{j+1,n}
\end{array}
\qquad
\begin{array}{c}
\phi_1 - f_a \\
\phi_2 \\
\phi_3 \\
- \\
- \\
\phi_{n-1} \\
\phi_n - f_b
\end{array}
$$

where

$$\gamma = -2 - \frac{2\,(\Delta x)^2}{\alpha\,(\Delta y)}$$

$$\phi_\kappa = \left[2 - \frac{2\,(\Delta x)^2}{\alpha\,(\Delta y)} \right] f_{j,k} - f_{j,k-1} - f_{j,k+1}$$

Exchanger Phase Reference Functions Implicit in Some Transport Models

Earlier in this literature review, exchange selectivities and exchanger phase reference functions which have been developed for the chemical study of exchange reactions were discussed. This section reviews the chemical submodels of solute transport models which simulate the transport of cationic solutes through reactive porous media. A chemical submodel of a solute transport model is defined here as that part of the solute transport model which describes the chemical reactions involving the solute. Most, though not all, of these chemical submodels of transport equations incorporate mass action equations and exchange selectivities. The exchanger phase reference functions which are implicit in the exchange selectivities used in these chemical submodels are typically different from those current in chemical reports of exchange reactions. Though all types of cationic solute chemical submodels will be reviewed here, most of the attention will be placed on chemical submodels which define exchange selectivities.

The chemical submodels found in published models of cation transport through porous media can be separated into three general categories: linearized, surface complexation, and exchange selectivity coefficient. Many sorption phenomena in soils have been found to approximate linearity and can be described successfully by a partition coefficient, K_d. Several authors (Nkedi-Kizza et al., 1984; Valocchi, 1984; Miller and Benson, 1983), while noting that ion exchange is frequently a non-linear phenomenon, have suggested that under certain conditions ion exchange reactions in solute transport models could be described by

$$c_i^s = K_d \, m_i^e \, .$$ [36]

The partition coefficient could be calculated from batch experiments (Nkedi-Kizza et al., 1984) or estimated from the exchange selectivity coefficients based implicitly on either mole fraction (Miller and Benson, 1983) or equivalent fraction (Valocchi, 1984) reference functions.

Recently, surface complexation models have been applied to models of cation transport. Cederberg et al. (1985) incorporated the surface complexation models available in MICROQL to solute transport equation named TRANQL. Jennings et al. (1982) applied the surface complexation model of Schindler et al. (1976) in their cation transport model.

The thermodynamic exchange constant relates the activities of the two cations in the exchanger and solution phases

$$K_{\mathrm{ex}i/j} = \left(\frac{a_i^e}{a_i^s}\right)^{z_j} \left(\frac{a_j^s}{a_j^e}\right)^{z_i}$$

where

$K_{\mathrm{ex}i/j}$ = thermodynamic exchange constant

a_i^e = activity of solute i in the exchanger phase

a_i^s = activity of solute i in the solution phase

z_i = valence of cationic solute i

By using the mathematical form of the thermodynamic exchange constant defining relation in establishing a chemical submodel, the developers of cation transport models are, consciously or unconsciously, using the resulting implicit exchanger phase reference function as an approximation of exchanger phase activity. Mole fraction, equivalent fraction, equivalent molality, Gapon, and mass ratio have all been used as exchanger phase reference functions.

Many authors have followed the seminal work of Rubin and James (1971) who defined their exchange selectivity coefficient (using the symbols of this study) as

$$k_{(RJ)i/j} = \left(\frac{m_{i'}^e}{c_{i'}^s}\right)^{z_j} \left(\frac{c_{j'}^s}{m_{j'}^e}\right)^{z_i}.$$

This coefficient uses the equivalent exchanger phase molality ($\frac{1}{z_i}$ mol kg-1) as the implicit exchanger phase reference function. This implicit reference function has been adopted also by Robbins et al. (1980), Cederberg et al. (1985), Charbeneau (1981), Barnes and Aylmore (1984), Rubin (1983), and Dutt et al. (1972). Among the selectivity coefficients used in soil chemistry, the Gaines-Thomas reference function is closest to the selectivity coefficient used by Rubin and James. The two selectivity coefficients are related by the relationship

$$k_{(GT)i/j} = z_i^{z_j} z_j^{-z_i} \, k_{(RJ)i/j} \, CEC^{(z_i - z_j)} \qquad [37]$$

where CEC is the cation exchange capacity of the porous medium.

Some authors have chosen the equivalent fraction as the exchanger phase reference function for exchange chemical submodels of solute transport models (Valocchi et al. 1981a and 1981b; Lai and Jurinak, 1971; and Meyers and Salter, 1984).

If we denote the exchange selectivity coefficient defined by the choice of the exchanger phase equivalent fraction and the solution phase normality as the Valocchi selectivity coefficient ($k_{(VAL)i/j}$)

$$k_{(VAL)i/j} = \left(\frac{x_{i'}^e}{c_{i'}^s}\right)^{z_j} \left(\frac{c_{j'}^s}{x_{j'}^e}\right)^{z_i} \qquad [38]$$

it is easy to show that this selectivity coefficient is related to the Rubin-James selectivity coefficient by

$$k_{(VAL)i/j} = k_{(RJ)i/j} \; CEC^{z_i - z_j}. \qquad [39]$$

Accordingly, the exchanger phase equivalent molality and exchanger phase equivalent fraction will be treated in this study as being functionally equivalent. For reasons of brevity, only the exchanger phase equivalent fraction and the Gaines-Thomas selectivity coefficient will be discussed, while the conclusions drawn for these representations apply directly to representations based on the exchanger phase equivalent molality reference function.

While the mole fraction reference function and the Vanselow selectivity coefficient which it defines have been used widely in investigations of ion exchange equilibria in batch systems, only one cation transport model (that used by Miller and Benson, 1983) explicitly uses that reference function.

Apparently most developers of cation transport models have found that the exchanger phase equivalent fraction reference function (or its analogue) is more straightforward to use in cation transport models than the exchanger phase

mole fraction reference function. This occurs because if the cation exchange capacity of the porous medium is assumed to be constant and the quantity of exchangeable cations expressed in numbers of equivalents, the sum of exchangeable cations per unit mass of the porous medium will always equal to the CEC, whereas the total number of moles of exchangeable cations will vary with exchanger phase composition. This difficulty could be overcome if the Gaines-Thomas selectivity coefficient (or its analogue) were allowed to vary as a function of exchanger phase composition. Even without considering variable Gaines-Thomas selectivity coefficients, these solute transport models are often very complex, so that the apparent inclination has been to hold the Gaines-Thomas selectivity coefficient (or its analogue) constant. Only Lai an his coworkers (Lai and Jurinak, 1972; and Lai et al., 1978) and Mansell et al. (1986) have considered exchange selectivities which vary with exchanger phase composition.

Thus two questions must be considered when models are used to describe cation transport in porous media: 1) what is the magnitude of error conveyed to predictions of cation movement in porous media by adoption of a particular exchanger phase reference function and 2) to what extent are transport model simulations improved by using exchange selectivities which vary with exchanger phase composition. This investigation was designed to provide answers for these questions using a simplified system of three cationic solutes

in columns packed with a mixture of quartz sand and synthetic exchange resin.

OBJECTIVES

It was assumed that all exchanger phase reference functions could describe exchange behavior equally well if a functional relation could be developed for the chosen reference function and exchanger phase composition. If the selectivity coefficient was set to a fixed value, however, which selectivity coefficient would give the most accurate description of exchange equilibria? The primary objective of this study was to determine which exchanger phase reference functions, when employed in a chemical submodel of a solute transport model, gave the most accurate description of cation movement in columns of porous media in systems involving ternary cation exchange.

The secondary objective was to determine if data from binary ion exchange experiments were sufficient for the accurate description of heterovalent ternary exchange isotherms and the accurate description of cation movement in columns of porous media in systems involving ternary cation exchange.

Three exchanger phase reference functions were evaluated in this study: the mole fraction, the equivalent fraction, and the statistical thermodynamic. The predictive utility of

33

these reference functions were to be evaluated for three capabilities: 1) to estimate accurately exchanger phase activity in binary exchange experiments; 2) when used to calculate binary and ternary cation exchange equilibria, to estimate accurately exchanger phase compositions; and 3) when incorporated in the chemical submodel of a solute transport model simulating the one-dimensional flow of three cations through a column packed with exchanging porous media, to predict accurately the distribution of cations in the column effluent.

Typically, binary exchange experiments must be conducted to determine the thermodynamic exchange constant. For accurate modeling of a ternary or higher order exchange system, however, the exchange constant alone is not sufficient and multicomponent exchange experiments should be conducted to augment the information obtained by binary exchange experiments. An addition objective of this study was to assess the increase in predictive accuracy ternary exchange information brought when used to calculate exchange equilibria both in batch ternary exchange experiments and in simulations solute concentrations in column experiments with three cations.

MATERIALS AND METHODS

Batch Determination of Binary and Ternary Exchange Isotherms

Materials

The ion exchanger used for these experiments was AG MP-50 Analytical grade Macroporous Cation Resin, 200-400 mesh, which was supplied by BioRad in hydrogen form. AG MP-50 is a sulphonic polystyrene-divinylbenzene strongly acidic cation exchanger with 8% crosslinking marketed by BioRad. The listed exchange capacity was 4.6 mol(+) kg^{-1} with a nominal surface of area of 35 m^2 g^{-1}. The lyotropic series of this exchanger for monovalent and divalent cations are (Dow Chemical Company, 1964):

$$Ba^{2+}>Pb^{2+}>Sr^{2+}>Ca^{2+}>Ni^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Zn^{2+}>Mg^{2+}>Be^{2+}$$

and

$$Ag^{1+}>Ti^{1+}>Cs^{1+}>Rb^{1+}>K^{1+}>NH_4^{1+}>Na^{1+}>H^{1+}>Li^{1+}.$$
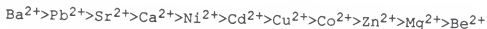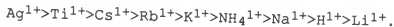
By comparison, the general lyotropic series of soils and clay minerals for monovalent and divalent cations are

$$Ba^{2+}>Sr^{2+}>Ca^{2+}+Mg^{2+}$$

and

$$H^{1+}>Ag^{1+}>Ti^{1+}>Cs^{1+}>Rb^{1+}>K^{1+}\approx NH_4^{1+}>Na^{1+}\approx Li^{1+}$$
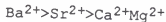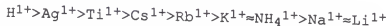
(Bohn et al., 1985).

The gross and fine microscopic structure of this type of exchanger are presented in Figures 1 and 2. For this type of exchanger at 25°, the standard free energy of the exchange reactions Ca→Na (meaning that the reaction product is Na-ion exchanger), Mg→Ca, and Na→Mg were found to be 1500, -2800, and -170 J mol^{-1}, respectively (Boyd, 1970). Perchlorate was chosen as the common anion because unlike chloride, perchlorate does not form monovalent ion pairs or complexes in solution with bivalent alkaline earth cations such as calcium and magnesium (Sposito et al., 1983). Three perchlorate salts were used in the experiments calcium perchlorate (Ca(ClO$_4$)$_2$·4H$_2$O, formula weight 371.06, supplied by GFS Chemicals), magnesium perchlorate (Mg(ClO$_4$)$_2$·6H$_2$O, formula weight 331.33, supplied by GFS Chemicals), and sodium perchlorate (NaClO$_4$·H$_2$O, formula weight 140.46, supplied by Fisher Scientific).

Seven exchange isotherms, four ternary and three binary, were determined by batch techniques. As discussed in the literature review, the value of the thermodynamic exchange constant may be estimated by integrating the values of the adjusted Vanselow selectivity coefficient from the two homoionic ion exchanger compositions, the exchanger phase equivalent fraction acting as the variable of integration. Accordingly, equilibrating solution compositions were chosen so that equilibria were established at regular intervals of the exchanger phase equivalent fraction. Since the exchange constants were not known, the expected exchanger phase
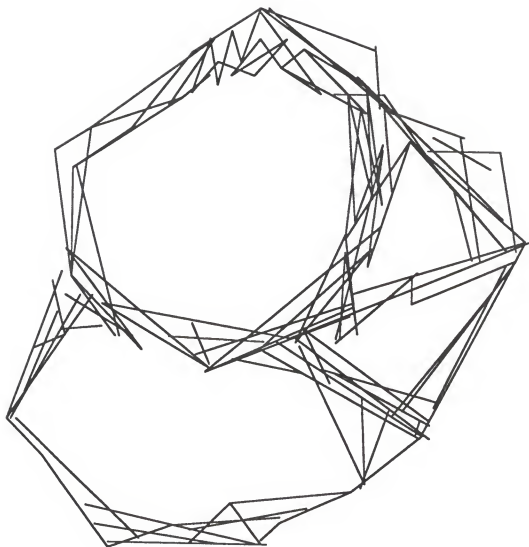
Figure 1. Generalized schematic microscopic drawing of a macroporous ion-exchange resin, showing the macropores. (After Grimshaw and Harland, 1975).
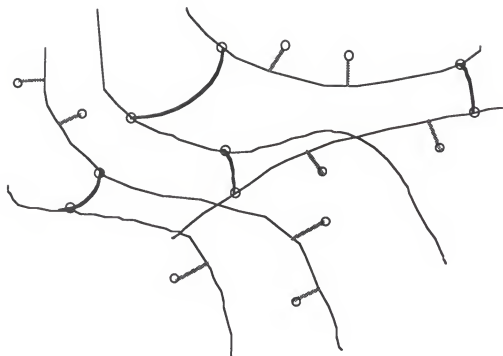
_____✦ Polystyrene chain

Divinylbenzene cross-linking

Sulphonic group

Figure 2. Schematic drawing showing
the microscopic structure of a
sulphonic divinylbenzene-polystyren
cation resin. (After Paterson, 1970)

compositions were only approximate. In establishing the equilibrating solution compositions, it was assumed that sodium was the cation least preferred of the three cations by the exchange resin and the ion exchange resin showed equal preference for calcium and magnesium ions. Target equilibrating solution cation equivalent fractions are presented in Tables 1 and 2.

Experimental Procedure

The batch and column experiments were performed in a laboratory in which the ambient temperature was maintained at $24.5 \pm 0.6°$ C. Each equilibration was replicated thrice. Each batch equilibration was conducted in a 50 cm^3 polycarbonate Oak Ridge centrifuge tube. After the centrifuge tubes were oven dried and allowed to cool over anhydrous calcium sulfate in an evacuated desiccator, the combined mass of each marked tube and its cap was determined to a 0.1 mg on a Mettler H80 balance. Approximately 0.1 g of AG MP-50 cation resin was placed in each tube. Since the mass of the equilibrating solutions, described in following paragraph, was approximately 20 g, the solids to solution ratio for these experiments was roughly 1:200. The first series of equilibrations was conducted to replace exchangeable hydrogen on the exchange sites with a cationic composition close to that of the final equilibrations. The cation resin was equilibrated with solutions prepared with the same rational composition as indicated in Tables 1 and 2, but with a

Table 1. Target cationic equivalent fractions for the ternary
exchange equilibrating solutions.

Set number	Equilibration	Cation		
		Ca	Mg	Na
		-------equivalent fraction-------		
One	A	0.720	0.180	0.100
	B	0.520	0.130	0.350
	C	0.280	0.070	0.650
	D	0.120	0.030	0.850
	E	0.100	0.025	0.875
	F	0.080	0.020	0.900
	G	0.060	0.015	0.925
	H	0.020	0.005	0.975
Two	A	0.540	0.360	0.100
	B	0.390	0.260	0.350
	C	0.210	0.140	0.650
	D	0.090	0.060	0.850
	E	0.075	0.050	0.875
	F	0.060	0.040	0.900
	G	0.045	0.030	0.925
	H	0.015	0.010	0.975
Three	A	0.360	0.540	0.100
	B	0.260	0.390	0.350
	C	0.140	0.210	0.650
	D	0.060	0.090	0.850
	E	0.050	0.075	0.875
	F	0.040	0.060	0.900
	G	0.030	0.045	0.925
	H	0.010	0.015	0.975
Four	A	0.180	0.720	0.100
	B	0.130	0.520	0.350
	C	0.070	0.280	0.650
	D	0.030	0.120	0.850
	E	0.025	0.100	0.875
	F	0.020	0.080	0.900
	G	0.015	0.060	0.925
	H	0.005	0.020	0.975

Table 2. Target cationic equivalent fractions for the binary
exchange equilibrating solutions.

Set number	Equilibration	Cation		
		Ca	Mg	Na
		--------equivalent fraction------		
Five	A	0.000	1.000	
	B	0.100	0.900	
	C	0.200	0.800	
	D	0.300	0.700	
	E	0.400	0.600	
	F	0.500	0.500	
	G	0.600	0.400	
	H	0.700	0.300	
	I	0.800	0.200	
	J	0.900	0.100	
	K	1.000	0.000	
Six	A	0.000		1.000
	B	0.025		0.975
	C	0.050		0.950
	D	0.075		0.925
	E	0.100		0.900
	F	0.125		0.875
	G	0.150		0.850
	H	0.350		0.650
	I	0.650		0.350
	J	0.900		0.100
	K	1.000		0.000
Seven	A		0.000	1.000
	B		0.025	0.975
	C		0.050	0.950
	D		0.075	0.925
	E		0.100	0.900
	F		0.125	0.875
	G		0.150	0.850
	H		0.350	0.650
	I		0.650	0.350
	J		0.900	0.100
	K		1.000	0.000

constant chloride concentration of 1.0 mol dm^{-3}. The cation resin was equilibrated with 40 cm^3 of the appropriate solutions. Because the effective mean diameter of the resin was large as compared with soil colloids, the resin settled to the bottom of the centrifuge tubes after a few moments, and centrifugation was not necessary. Once the resin had settled to the bottom of the centrifuge tube, the supernatant solution was decanted and a fresh 20 cm^3 of solution were added to the centrifuge tubes. The equilibration and decantation were repeated until the pH of the supernatant solution was greater than 6.0, which was achieved typically after seven equilibrations. After this, the pH of the equilibrating solution was not monitored further. While Sposito and Fletcher (1986) have argued that H$^+$ may be considered as an exchangeable cation in some soil systems, the pK$_a$ of the sulphonic surface functional group of the cation resin is 2 and thus it may be safely assumed that H$^+$ cations were absent from the exchange complex during the column and batch experiments (Kunin, 1972). The resin was then equilibrated with four rinses of deionized water. The resin was then equilibrated eight times with 20 cm^{-3} of salt solutions having rational cationic compositions indicated in Tables 1 and 2, but with a constant perchlorate concentration of 0.01 mol dm^{-3}. The supernatant solution of the final equilibration was retained and the combined mass of the cap and the centrifuge tube containing the resin and entrained perchlorate solution was measured to an accuracy of 0.01 g

with a Mettler digital balance. The centrifuge tubes containing the resin and entrained solution were then oven-dried, allowed to cool over calcium sulfate in an evacuated desiccator and weighed to the nearest 0.1 mg. The resin was then extracted by five washings of 20 cm^3 1.0 mol dm^{-3} ammonium acetate ($NH_4C_2H_3O_2$). The supernatant from each washing was poured into a 100 cm^3 volumetric flask, which was brought to volume after the final washing. The extracted solutions were filtered to remove any resin which found its way into the volumetric flask and stored in 125 cm^3 Nalgene rectangular high-density polyethylene bottles until analysis.

Equilibrium and extracted solutions were diluted in duplicate to yield solutions to analyze for calcium, magnesium, and sodium. All chemical analyses of the equilibrium and extractant solutions were performed on a Perkin-Elmer 460 Atomic Absorption Spectrophotometer. Calcium in solution was determined by atomic absorption flame spectrometry (Willard et al., 1981; Perkin-Elmer Corporation, 1976). A Perkin-Elmer Intensitron™ Lamp (#303-6017) was the light source. A nitrous oxide-acetylene flame flame was used. Absorbance was measured at 422.7 nm. Magnesium was analyzed by atomic absorption flame spectrometry. An acetylene-air flame was used. A Perkin-Elmer Intensitron™ Lamp (#303-6042) was the light source. Absorbance was measured at 285.2 nm. Sodium was determined by flame emission spectrometry. An acetylene-air flame was used. Emission was measured at 589.6 nm.

Data Analyses

Gravimetric data were used to calculate the weight of the oven dry cation resin and the weight of the entrained solution. The chemical analyses yielded the concentrations of calcium, magnesium, and sodium in the equilibrating solutions and the extractant solutions. Concentrations of the ions in the equilibrating solutions were taken to be that in entrained solutions. The following formula was used to calculate the molalities of each ion in the exchanger phase:

$$m_i^e = \frac{V(\text{v.f.})\, c_i^S(\text{extr.}) - V(\text{entr.})\, c_i^S(\text{equil.})}{m(\text{resin})}$$

where

$V(\text{v.f.})$ = volume of the volumetric flask (dm^3)

$V(\text{entr.})$ = volume of the entrained solution (dm^3)

$c_i^S(\text{extr.})$ = concentration of cation i in the extractant solution (mol dm^{-3})

$c_i^S(\text{equil.})$ = concentration of cation i in the final supernatant equilibrating solution (mol dm^{-3})

$m(\text{resin})$ = mass of the resin

The mean liquid phase and surface phase concentrations for the three replications were used to for all further calculations. The liquid phase activity coefficient is estimated by the Davies equation

$$\ln \gamma_i = -A_\gamma z_i^2 \left(\frac{I_c^{1/2}}{1 + I_c^{1/2}} - 0.2\, I_c \right)$$

where

γ_i = is the solution phase cation activity coefficient,

A_γ = Debye-Hückel parameter,

I_c = ionic strength of the electrolyte solution,

(concentration basis)

$= \dfrac{1}{2} \displaystyle\sum_{k=1}^{n} z_k^2 c_k$, and

z_k = valence of cation or anion.

(Sposito, 1981b).

These data were used to calculate Vanselow, Gaines-Thomas, and statistical thermodynamic adjusted selectivity coefficients.

Quadratric regressions were performed for the relation between $\ln k_{(V)i/j}^a$, $\ln k_{(GT)i/j}^a$, $\ln k_{(ST)i/j}^a$ and the surface phase equivalent fraction of the cation j. The regression between $\ln k_{(V)i/j}$ and the surface phase mole fraction was used to evaluate the integral

$$\ln K_{exi/j} = \int_0^1 \ln k_{(V)i/j}^a \, dx_j^e \; .$$

Binary and ternary regression parameters were adjusted so that the triangle rule appropriate for thermodynamic exchange constants was obeyed (Helfferich, 1962).

Column Experiments Used to Assess Chemical Submodels

Materials

An empty stainless steel HPLC column, 50.0 cm long with a 2.54 cm outside diameter, and 2.25 cm inside diameter was used for column experiments. Columns of this size are typically used as preparative HPLC columns. The column packing was a 1:250 (w:w) mixture of AG MP-50 Analytical grade Macroporous Cation Resin and pure quartz sand derived from a soil sample removed from the E2 horizon, at a depth 45 to 70 cm in a soil classified as a St. Lucy fine sand (Location of pit NW 1/4 of SE 1/4 Sec. T32S R20E). The soil sample was sieved and any organic material was oxidized by repeated washings with 30% (volume:volume) H_2O_2. Mariotte bottles were made from 1 dm^3 Wheaton "400" brand borosilicate glass serum bottle. A Rainin Rabbit Peristaltic pump (Rainin Instrument Co., Inc.;Mack RD; Woburn, MA 01801) mounted with Fisherbrand PVC Manifold Tubing with a 1.85 mm inside diameter was used to drive the solutions through the packed column. Aside from the manifold tubing, all tubing was Tygon™ Clear laboratory tubing (3.2 mm inside diameter, 6.4 mm outside diameter). Choice of column influent was made by using a Pharmacia solvent resistant valve SRV-3(supplied by Pharmacia Inc.; 800 Centennial AV; Piscataway, NJ 08854). The flow rate was always 0.0167 g s^{-1} (1 g min^{-1}). This corresponds to a nominal linear flow rate of 4.20×10^{-5} m s^{-1} and an interstitial velocity of 1.31×10^{-4} m s^{-1}.

Experimental Procedure

Determination of column CEC

The column was saturated with 0.01 mol $(NaClO_4)$ dm^{-3} solution. The mass of the column was determined. The influent solution was changed to a 0.01 mol $(1/2 \; Ca(ClO_4)_2)$ dm^{-3} solution. Fractions of the column effluent were collected. Sodium in these factions was determined by flame emission spectrometry. The column CEC (mol (Na^{1+})) was taken to be the total Na eluted (mol Na^{1+}) less the Na in solution in column before displacement by Ca^{2+} (mol Na^{1+}).

Determination of mass of solids

The empty column including the tube, frits, ferrules, end fitting bodies, nuts and plastic male column end caps, was weighed. The packed column was oven-dried until the measured mass of the packed column reached a constant (to a tenth of a gram) value. The mass of solids was taken to be the mass of oven-dry packed column less those of the empty column and the end fitting bodies

Determination of porosity

As noted above, the majority of the column packing was quartz sand. Wilding et al.(1977) cited a value of 2.65 kg dm^{-3} for the density of quartz. The porosity (Scheidegger, 1972) was therefore

porosity = (total volume - (particle
weight/particle density))/total volume

Determination of volumetric water content

The mass of the water-filled packed column was
determined after every run. The volumetric water content was
calculated by

Volumetric water content = Total volume -
((Total mass - mass column -
mass solids)/density of water)

Column Experiments

All column experiments were conducted in a laboratory
with ambient temperature at 24.5 ± 0.6 C°. A schematic of the
arrangement of the equipment used in the column experiments
is presented in Figure 3.

First case, Run A. All solutions passing through the
column were saturated with He gas to reduce the formation of
air bubbles in the column by cavitation. At least 15 pore
volumes of 0.01 mol($1/2$ Ca(ClO$_4$)$_2$) dm^{-3} solution were passed
through the column with a flow rate of 1 g min^{-1}. The pump
was stopped momentarily so that the influent stream could be
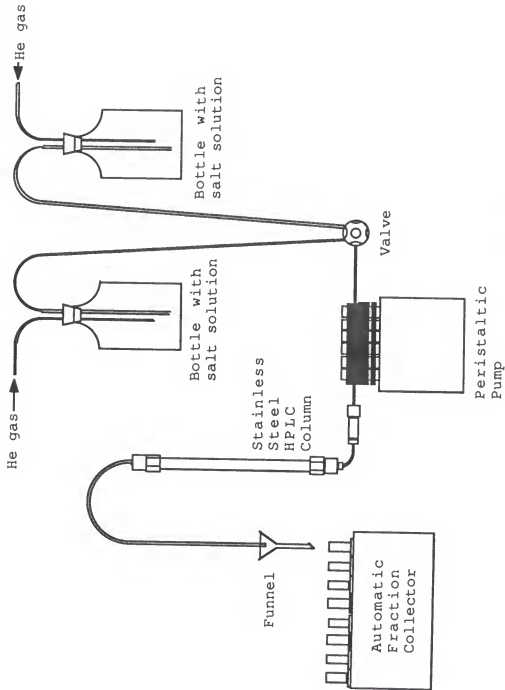
Figure 3. Schematic of equipment arrangement for column experiments

changed to a solution containing 0.005 mol (1/2 Mg(ClO$_4$)$_2$) dm^{-3} 0.005 mol(NaClO$_4$)dm^{-3} solution. After 61 minutes, the influent flow was reverted to 0.01 mol(1/2 Ca(ClO$_4$)$_2$) dm^{-3} solution. Fifty-five fractions of the effluent of approximately 10 g were collected. The solution concentrations of Ca, Mg, and Na were determined for each effluent sample by the methods described in the section of this chapter describing the batch exchange determinations.

Second case, Run B. All solutions passing through the column were saturated with He gas to reduce the formation of bubbles in the column by cavitation. At least 15 pore volumes of 0.01 mol(NaClO$_4$) dm^{-3} solution were passed through the column at a flow rate of 1 g min^{-1}. The pump was stopped momentarily so that the influent stream could be change to a solution containing 0.005 mol(1/2 Ca(ClO$_4$)$_2$)dm^{-3} 0.005 mol(1/2 Mg(ClO$_4$)$_2$) dm-3 solution. After 61 minutes, the influent flow was reverted to 0.01 mol(1/2 Ca(ClO$_4$)$_2$) dm^{-3} solution. Fifty-nine fractions of the effluent of approximately 10 g were collected. Solution concentrations of Ca, Mg, and Na were determined by the methods described in the section of this chapter describing the batch exchange determinations.

COMPUTER MODEL DEVELOPMENT

Two computer programs were used in the evaluation of
three exchanger phase reference functions for inclusion as
chemical submodels of cation transport models. The first
computer program, named BLCKBX (Black box), calculated the
binary and ternary isotherms dictated by the thermodynamic
exchange constants, solution phase and exchanger phase
activity coefficients. The exchange isotherms calculated by
Program BLCKBX were used, along with appropriate initial and
boundary conditions, in the second program, TABMODEL (Tabular
model), to calculate cation transport. Two separate programs,
rather than one integrated program, were developed because it
was found to be more efficient computationally to calculate a
complete exchange isotherm before attempting to solve the
solute transport problem. The development and uses of these
programs will be discussed below.

The Computer Program BLCKBX

Program BLCKBX is a FORTRAN computer program developed
to calculate instantaneous partitioning of three cations of
known amounts between the exchanger and solution phases. A

listing of this program is presented as an appendix to this dissertation. The program was used to calculate equilibrium exchange isotherms to be used to represent chemical submodels in convective-dispersive (advective-dispersive) transport models of systems involving steady state fluid flow through porous media.

The program BLCKBX calculated ternary exchange equilibria constrained by charge and mass balance in the exchanger and solution phases. Briefly, for each iteration, one of the exchange selectivity coefficients was used to estimate the distribution coefficient of one of the cations. The <u>distribution</u> <u>coefficient</u> (d_i) is the ratio of a cation in the exchanger phase to its concentration in the solution phase or

$$d_i = \frac{m_i^e}{c_i^s} \qquad [40]$$

where

c_i^s = cation i solution phase concentration (mol dm^{-3}),

and

m_i^e = cation i exchanger phase molality (mol kg^{-1}).

Since the total amount was specified as input, the solution phase concentration and exchanger phase molality of the cation in the two phases could be calculated directly. The solution phase concentration and exchanger phase molality of the other cation in the exchange selectivity coefficient were calculated by difference. These estimates were then used

to calculate the distribution coefficient in the next iteration. The program allowed the selection of one of three exchanger phase reference functions: the mole fraction used in the Vanselow (1932) formulation, the equivalent fraction found in the work of Gaines and Thomas (1953), and the statistical thermodynamic suggested by Krishnamoorthy et al. (1948).

Input to Program BLCKBX

An example of an input file for program input is included as an appendix to this dissertation. Aside from variables which specify the iterative tolerances and iterative limits of the computer program, seven variables or groups of variables were specified for each implementation of the program:

1. Porous medium bulk density (BULKD) in kilograms per cubic decimeter;

2. Volumetric water content (THETA) in cubic decimeters per cubic decimeter;

3. Cation exchange capacity (CECFIX) in moles (+) per kilogram;

4. The sum charge born by all cations in solution (CTOTAL) in moles(+) per cubic decimeter;

5. The three thermodynamic exchange constants (RKIJ0, RKJK0, and RKKI0; corresponding to $K_{exi/j}$, $K_{exj/k}$, and $K_{exk/i}$, respectively) which were dimensionless;

6. The valences (ZI, ZJ, and ZK) of each cation;

7. The total moles of each cation in the exchanger-solution system (CCI,CCJ,CCK) in moles per cubic decimeter.

Inclusion of Variable Selectivities and Activity Coefficients

In general, exchange selectivities are not fixed, but vary with changes in the composition of the exchanger phase. Estimates of these changes could be included in the calculation of exchange equilibria by several means. Three subroutines could be used to introduce estimates of exchanger phase and solution phase activity coefficients or exchange selectivities which vary with changes in the exchanger phase or solution phase composition. The exchanger phase and solution phase coefficients were called FI, FJ, or FK and GAMMAI, GAMMAJ, or GAMMAK, respectively. Every time the defining relations were used in a calculation, the values of the exchanger phase or solution phase activity coefficients could be adjusted by calling SUBROUTINE F, SUBROUTINE GAMMA, and SUBROUTINE KCALC. SUBROUTINE KCALC calculated the exchange selectivity coefficient. If the exchanger phase activity coefficients were not estimated, SUBROUTINE KCALC could be used to insert exchange selectivity coefficient values estimated by least-squares regression of the relationship between the ion exchange selectivity coefficients to the exchanger-solution system composition. If one had a regression equation relating the natural logarithm of the Vanselow selectivity coefficient, ln $k_{(v)i/j}$, and the exchanger phase cation i equivalent fraction and a

second regression equation relating ln $k_{(v)j/k}$ to exchanger
phase cation k equivalent fraction, the third ion exchange
selectivity coefficient, $k_{(v)k/i}$, could be calculated by the
triangle rule, one form of which states that

$$z_k \ln k_{(v)i/j} + z_i \ln k_{(v)j/k} + z_j \ln k_{(v)k/i} = 0 \qquad [41]$$

The three estimates of the ion exchange selectivity
coefficients could be calculated within SUBROUTINE KCALC,
each iteration of the main program being adjusted as the
estimated exchanger phase composition was changed. While all
implementations of variable exchange selectivities described
in this study used a variable adjusted Vanselow selectivity
coefficient, that is the value of the adjusted Vanselow
selectivity coefficient varied as a function of the exchanger
phase composition; in principle, the same results could be
achieved using other variable selectivities. The program
presented the solution phase concentrations and exchanger
phase molalities (in moles per decimeter and moles per
kilogram, respectively) as output.

The Steps in the Program BLCKBX Algorithm

The steps in the algorithm are given below.

Step 1. Given the ratios of cation exchange capacity
(CEC) and charge born by all cations in solution, the program
gave first estimates of the exchanger phase and solution
phase concentrations.

$$d_i(\text{est}) = \frac{\text{CEC}}{c_{\Sigma_+}^s} \qquad\qquad [42]$$

where

$c_{\Sigma_+}^s$ = sum of the charge born by all cations in solution (mol(+) dm^{-3})

Step 2. Based on the estimated distribution coefficients, the program calculated initial values of the exchanger phase and solution phase concentrations of all cations.

$$c_i^s = \frac{N_i}{\rho_b \, d_i + \theta} \qquad\qquad [43]$$

$$m_i^e = \frac{N_i}{\frac{\theta}{d_i} + \rho_b} \qquad\qquad [44]$$

where N_i = total concentration of cation solute i in both the exchanger and solute phases (mol dm^{-3})

$$N_i = \rho_b \, m_i^e + \theta \, c_i^s \qquad\qquad [45]$$

Step 3. Using the initial values of the exchanger phase and solution phase concentrations, the program recalculated the distribution coefficient for one of the ions

$$d_i = \frac{\gamma_i}{f_i} \left(\frac{f_j m_j^e}{\gamma_i c_i^s}\right)^{\left(\frac{z_i}{z_j}\right)} D_i^{\left(\frac{z_i}{z_j} - 1\right)} K_{\text{exi}/j}^{\frac{1}{z_j}} \qquad\qquad [46]$$

Step 4. Based on the estimated distribution coefficients, the program calculated initial values of the exchanger phase and solution phase concentrations of all cations

$$c_i^s = \frac{N_i}{\rho_b \, d_i + \theta}$$

$$m_i^e = \frac{N_i}{\frac{\theta}{d_i} + \rho_b}$$

Step 5. Using these exchanger phase and solution phase concentrations, the program calculated by difference the exchanger phase and solution phase concentrations of the other cation in the defining relation.

$$m_j^e = \frac{CEC - \displaystyle\sum_{k \neq i; j}^{n} z_k m_k^e - z_i m_i^e}{z_j} \qquad [47]$$

$$c_j^s = \frac{c_{\Sigma+}^s - \displaystyle\sum_{k \neq i; j}^{n} z_k c_k^s - z_i c_i^s}{z_j} \qquad [48]$$

Step 6. The program then checked to determine if both m_j^e and c_j^s were greater than zero.

If the two were greater than zero, Steps 3-6 were

repeated until the estimated exchanger phase composition converged to an acceptable absolute difference between iterations. (Please note that during the solution of the exchanger phase composition using $K_{exi/j}$ the concentrations of all cations other than cation i and cation j were fixed; that is, the sums

$$\sum_{k \neq i;j}^{n} z_k m_k^e \text{ , and}$$

$$\sum_{k \neq i;j}^{n} z_k c_k^s$$

in equations [47] and [48] were fixed. The other cations were allowed to vary (and thus have their exchanger phase and solution phase concentrations estimated) by following the same Steps 1-6 but using with different thermodynamic exchange constants (e.g. $K_{exj/k}$ or $K_{exk/i}$).)

If one of the two was not greater than zero, the program assigned c_j^s , m_j^e , c_i^s , and m_i^e their previous values and used the same defining relationship to estimate d_j (instead of d_i) and the Steps 4-6 were carried out with roles of cation i and cation j reversed. If, at Step 6, c_i^s and m_i^e were not greater than zero the program went to Step 7 and selected another defining relation (e.g. $K_{exj/k}$) to estimate iteratively the exchanger phase composition.

For an n-ary system (i.e. one with n cations) there are $2*n$ possible iterative loops; only $n-1$ iterative loops need converge to estimate the exchanger phase composition.

Step 7. Once the estimates for the defining relation involving $K_{exi/j}$ have been resolved, the program performed Steps 1-6 using another ion exchange constant. As before, the program checked for convergence and non-negative estimated exchanger phase and solution phase concentrations.

Step 8. The program repeated Step 7 until $n-1$ defining relations had been resolved.

Step 9. The program used the resulting estimates of solution phase and exchanger phase compositions as the input for a repetition of Steps 3-8 until the estimated exchanger phase composition converged to an acceptable absolute difference between iterations.

For reproducible estimates, meaning predicted isotherms which are identical regardless of the order in which the defining relations were chosen in the algorithm, the tolerance used to judge convergence of exchanger phase composition had to be on the order of 10^{-8}. This caused millions of iterations to be performed so that the resolution of a ternary isotherm consisting of 2500 distinct fractions of cationic amounts could take 1.5 hours of central processing unit (CPU) time on a Digital Equipment Corporation VAX 11/750 minicomputer having a floating point coprocessor. No attempt to optimize execution time while preserving reproducibility was attempted.

The accuracy of BLCKBX as a method of calculating ternary, heterovalent exchange equilibria was checked by three tests. First, the output of the program maintained overall cation mass balance between the exchanger and solution phases, and maintained charge balance in both the solution and exchanger phases. Second, the calculated cation exchanger phase molalities and cation solution phase concentrations consistently reproduced each of the appropriate exchange selectivity coefficients. Third, program BLCKBX generated the same exchange isotherm irrespective of the order by which the defining relations were solved within the program.

The Computer Program TABMODEL

The second computer program, TABMODEL, used the isotherms generated by BLCKBX to solve the simultaneous one-dimensional transport of three cationic solutes through porous media. The program was developed by S.A. Bloom and R.S. Mansell of the Soil Science Department, University of Florida. The program TABMODEL used a tabular look-up method of solving the one-dimensional convective dispersive equation for multicomponent cation transport through porous media. The convective-dispersive (advective-dispersive) equation

$$\frac{\delta c_i^s,}{\delta t} + \frac{\rho_b}{\theta} \frac{\delta m_i^e,}{\delta t} = D \frac{\delta^2 c_i^s,}{\delta z^2} - u \frac{\delta c_i^s,}{\delta z} \qquad [2]$$

was approximated numerically according to the
Crank-Nicholson convention by

$$c_i^s,(z, n+1) - c_i^s,(z, n)$$

$$= \frac{\Delta t \; D}{2 \Delta z^2} \left[c_i^s,(z-1, n+1) - 2c_i^s,(z, n+1) + c_i^s,(z+1, n+1) \right.$$

$$\left. + c_i^s,(z-1, n) - 2c_i^s,(z, n) - c_i^s,(z+1, n) \right]$$

$$- \frac{\Delta t \; v}{4 \Delta z} \left[c_i^s,(z+1, n+1) - c_i^s,(z-1, n+1) + c_i^s,(z+1, n) \right.$$

$$\left. - c_i^s,(z-1, n) \right]$$

$$- \frac{\rho_b}{\theta} \; (m_i^e,(z, n+1) - m_i^e,(z, n)) \qquad [49]$$

By collecting terms, this could be represented by

$$c_i^s,(z-1, n+1) \left[-\frac{\Delta t \; D}{2 \Delta z^2} - \frac{\Delta t \; v}{4 \Delta z} \right] + c_i^s,(z, n+1) \left[1 + \frac{\Delta t \; D}{\Delta z^2} \right]$$

$$+ c_i^s,(z+1, n+1) \left[-\frac{\Delta t \; D}{2 \Delta z^2} + \frac{\Delta t \; v}{4 \Delta z} \right] =$$

$$c_i^s,(z-1, n) \left[\frac{\Delta t \; D}{2 \Delta z^2} + \frac{\Delta t \; v}{4 \Delta z} \right] + c_i^s,(z, n \;) \left[1 - \frac{\Delta t \; D}{\Delta z^2} \right]$$

$$+ c_i^s,(z+1, n) \left[\frac{\Delta t \; D}{2 \Delta z^2} - \frac{\Delta t \; v}{4 \Delta z} \right] - \frac{\rho_b}{\theta} \; m_i^e,(z, n+1) - m_i^e,(z, n)$$

$$[50]$$

As in the example in the literature review, this formulation was in turn converted to matrix form and solved by matrix multiplication.

This algorithm differed from other approaches in that the solution of the solution phase concentration depended on the final equilibrium concentration. There were four basic steps in the solution of the algorithm:

1. Calculate estimate of $c_i^s,(z,n+1)$ based, in first iteration in a loop $m_i^e,(z,n+1) = m_i^e,(z,n)$ is accepted; in later iterations the estimate of $m_i^e,(z,n+1)$ was based on the estimate resulting from the previous iteration;

2. Using the solution and exchanger phase concentrations the program calculated total cation concentration in an element;

3. Using an isotherm calculated in advance by program BLCKBX, the program calculated equilibrium distributions of the three cations in the exchanger and solution phases;

4. The program then used the resulting estimate of exchanger phase composition to present a new estimate of $m_i^e,(z,n+1)$.

The algorithm used the new estimate of exchanger phase composition and performed steps 1-4 until convergence. The user of the computer program was free to choose any method for calculating the equilibria which gave the estimates of $m_i^e,(z,n+1)$. This freedom allowed the evaluation of both

variable selectivity and several exchanger phase reference functions for the prediction of cation transport in ternary systems.

As will be shown later, the combination of these two computer programs was able to duplicate accurately experimental column data and the simulations based on an algorithm suggested by Valocchi et al. (1981b).

RESULTS AND DISCUSSION

Batch Experiments

Measured supernatant solution concentrations and exchangeable cation contents from all replicates of the exchange experiments with the cation resin are presented in Tables 3 through 9. Mean values of supernatant solution concentrations and exchangeable cation mole fractions for each equilibration composition are presented in Tables 10 and 11. These mean data were used in all subsequent analyses of the batch exchange data. The data reported by Elprince et al. (1980), who measured NH_4^{1+}- Ba^{2+}-La^{3+} exchange equilibria on montmorillonite shaken with salt solutions having constant 0.1 mol dm^{-3} Cl concentrations, were used to compare ternary exchange on natural exchangers with ternary exchange on synthetic exchangers.

Vanselow coefficient on exchanger phase equivalent fraction regression

The adjusted Vanselow selectivity coefficients were calculated for binary and ternary exchange experiments with the cation resin and those with montmorillonite reported by Elprince et al. (1980). For both groups of binary exchange

Table 3. Experimental exchange data for Set One.

Equilibration	Replication	Supernatant cation concentration			Exchangeable cation content		
		Ca	Mg	Na	Ca	Mg	Na
		------- mmol dm^{-3} -------			------- mmol -------		
A	1	3.255	0.993	1.266	0.169	0.008	0.002
A	2	3.795	0.992	1.292	0.171	0.007	0.005
A	3	3.838	0.989	1.256	0.180	0.007	0.001
B	1	2.842	0.757	4.018	0.171	0.010	0.008
B	2	2.881	0.756	4.001	0.185	0.010	0.006
B	3	2.889	0.762	4.035	0.170	0.010	0.007
C	1	1.338	0.387	7.325	0.167	ND	0.009
C	2	1.334	0.390	7.291	ND	0.009	ND
C	3	1.335	0.389	7.325	0.147	0.011	0.014
D	1	0.855	0.186	9.527	0.171	0.012	0.024
D	2	0.898	0.201	9.836	0.159	0.015	0.022
D	3	0.847	0.196	9.784	0.154	0.015	0.042
E	1	0.629	0.123	9.939	0.156	0.016	0.034
E	2	0.636	0.124	10.14	0.155	0.015	0.047
E	3	0.677	0.129	10.09	0.154	0.018	0.030
F	1	0.539	0.119	10.65	0.150	0.018	0.051
F	2	0.522	0.121	10.88	0.144	0.018	0.052
F	3	0.102	0.068	11.05	0.120	0.018	0.102
G	1	0.112	0.065	11.16	0.121	0.017	0.111
G	2	0.113	0.062	11.26	0.118	0.007	0.103
G	3	0.011	0.003	11.56	0.057	0.007	0.275
H	1	0.011	0.003	11.28	0.057	0.007	0.261
H	2	0.010	0.003	11.28	0.052	0.007	0.261
H	3	0.010	0.003	11.41	0.051	0.007	0.266

Table 4. Experimental exchange data for Set Two.

Equilibration	Replication	Supernatant cation concentration			Exchangable cation content		
		Ca	Mg	Na	Ca	Mg	Na
		mmol dm^{-3}			mmol		
A	1	2.980	1.947	1.191	0.304	0.048	0.004
A	2	2.936	1.933	1.170	0.312	0.049	0.002
A	3	2.938	1.901	1.181	0.287	0.045	0.001
B	1	2.037	1.381	3.938	0.324	0.047	0.010
B	2	2.038	1.39	3.848	0.304	0.044	0.011
B	3	2.065	1.394	3.938	0.302	0.044	0.009
C	1	1.062	1.044	7.455	0.299	0.050	0.027
C	2	1.087	1.043	7.243	0.315	0.050	ND
C	3	1.109	1.043	7.623	0.307	0.049	0.047
D	1	0.365	0.408	10.18	0.264	0.082	0.105
D	2	0.317	0.362	10.26	0.198	0.063	0.068
D	3	0.344	0.401	10.21	0.317	0.050	ND
E	1	0.209	0.310	10.62	0.204	0.079	0.135
E	2	0.206	0.309	10.62	0.192	0.076	0.189
E	3	0.119	0.298	10.52	0.333	0.115	ND
F	1	0.137	0.196	10.93	0.186	0.064	0.190
F	2	0.177	0.220	10.91	0.178	0.063	0.191
F	3	0.063	0.170	10.55	0.18	0.063	0.174
G	1	0.076	0.155	10.66	0.141	0.050	0.639
G	2	0.059	0.206	10.68	0.148	0.035	0.292
G	3	0.030	0.016	10.87	0.091	0.020	0.129
H	1	0.030	0.016	11.04	0.052	0.020	0.458
H	2	0.030	0.015	11.04	0.052	0.019	0.480
H	3			10.93	0.055	0.020	0.660

Table 5. Experimental exchange data for Set Three.

Equilibration	Replication	Supernatant cation concentration			Exchangeable cation content		
		Ca	Mg	Na	Ca	Mg	Na
		------------	mmol dm^{-3}	------------	------------	mmol	------------
A	1	1.832	2.941	1.219	ND	0.087	ND
A	2	1.881	2.944	1.240	0.328	0.087	0.004
A	3	1.852	2.864	1.203	0.327	0.108	0.007
B	1	1.326	2.076	4.093	0.314	0.082	0.014
B	2	1.308	2.029	4.084	ND	ND	ND
B	3	1.311	1.932	4.102	0.308	0.095	0.016
C	1	0.637	1.252	7.575	ND	0.106	0.034
C	2	0.691	1.254	7.257	0.296	0.106	0.030
C	3	0.681	1.186	7.184	0.305	0.115	0.035
D	1	0.152	0.233	9.814	0.185	0.112	0.049
D	2	0.145	0.208	9.868	0.212	0.156	0.103
D	3	0.145	0.212	9.814	0.213	0.140	0.096
E	1	0.078	0.234	10.25	0.198	0.146	0.220
E	2	0.087	0.220	10.33	0.188	0.140	0.175
E	3	0.094	0.252	10.39	0.198	0.076	0.151
F	1	0.032	0.146	10.49	0.148	0.114	0.203
F	2	0.028	0.129	10.52	0.161	0.124	0.214
F	3	0.036	0.136	10.65	0.151	0.113	0.246
G	1	0.036	0.041	10.45	0.124	0.084	0.324
G	2	0.037	0.042	10.50	0.131	0.090	0.327
G	3	0.037	0.035	10.50	0.117	0.083	0.300
H	1	0.019	0.024	10.84	0.050	0.026	0.459
H	2	0.019	0.023	10.73	0.057	0.030	0.543
H	3	0.018	0.022	10.67	0.055	0.031	0.529

Table 6. Experimental exchange data for Set Four.

Equilibration	Replication	Supernatant cation concentration			Exchangable cation content		
		Ca	Mg	Na	Ca	Mg	Na
		mmol dm^{-3}			mmol		
A	1	0.899	3.443	1.136	0.228	0.170	0.006
A	2	0.896	3.716	1.122	0.221	0.168	0.005
A	3	0.909	3.617	1.105	0.220	0.161	0.005
B	1	0.616	2.896	3.884	0.221	0.165	0.016
B	2	0.604	2.848	3.686	0.222	0.169	0.017
B	3	0.619	2.753	4.072	0.466	0.171	0.017
C	1	0.313	1.496	7.291	0.165	0.127	0.028
C	2	0.301	1.517	7.065	0.182	0.147	0.032
C	3	0.316	1.406	6.672	0.194	0.165	0.039
D	1	0.055	0.439	9.332	0.131	0.212	0.175
D	2	0.048	0.343	9.667	0.129	0.209	0.179
D	3	0.049	0.416	9.723	0.133	0.202	0.138
E	1	0.071	0.279	9.695	0.108	0.184	0.145
E	2	0.069	0.264	9.695	0.089	0.153	0.147
E	3	0.052	0.189	10.11	0.097	0.164	0.206
F	1	0.046	0.171	10.73	0.098	0.159	0.205
F	2	0.053	0.191	11.01	0.091	0.158	0.178
F	3	0.055	0.193	10.39	0.042	0.067	0.071
G	1	0.050	0.141	10.95	0.037	0.106	0.111
G	2	0.044	0.121	11.52	0.062	0.112	0.225
G	3	0.062	0.153	10.66	0.057	0.082	0.261
H	1	0.018	0.037	10.80	0.014	0.026	0.411
H	2	0.019	0.040	11.18	0.009	0.030	0.377
H	3	0.019	0.040	10.55	0.003	0.039	0.245

Table 7. Experimental exchange data for Set Five

Equilibration	Replication	Supernatant cation concentration		Exchangable cation content	
		Ca	Mg	Ca	Mg
		----mmol dm^{-3}---		------mmol-----	
A	1	5.028	0.000	0.344	0.000
A	2	5.087	0.000	0.293	0.000
A	3	5.087	0.000	0.303	0.000
B	1	0.162	4.440	0.116	0.216
B	2	0.173	4.407	0.120	0.219
B	3	0.170	4.351	0.119	0.218
C	1	0.964	4.144	0.249	0.180
C	2	1.006	4.110	0.232	0.168
C	3	0.996	4.092	0.229	0.172
D	1	1.471	3.695	0.256	0.111
D	2	1.474	3.644	0.262	0.124
D	3	1.452	3.585	ND	ND
E	1	1.958	3.187	0.304	0.094
E	2	1.927	3.160	0.296	0.086
E	3	2.006	3.201	0.289	0.078
F	1	0.000	2.683	0.361	0.052
F	2	0.000	2.729	0.274	0.045
F	3	0.000	2.706	0.293	0.044
G	1	2.930	2.132	0.292	0.043
G	2	2.867	2.132	0.340	0.049
G	3	2.880	2.081	0.353	0.050
H	1	3.417	1.637	0.291	0.027
H	2	3.369	1.643	0.362	0.036
H	3	3.327	1.643	0.329	0.033
I	1	3.840	1.189	0.353	0.021
I	2	3.933	1.130	0.335	0.021
I	3	3.865	1.130	0.321	0.022
J	1	4.332	0.565	0.309	ND
J	2	4.216	0.571	0.270	0.008
J	3	4.139	0.568	0.364	ND
K	1	4.759	ND	ND	ND
K	2	4.811	ND	ND	ND

Table 8. Experimental exchange data for Set Six.

Equilibration	Replication	Supernatant cation concentration		Exchangable cation content	
		Ca	Na	Ca	Na
		----mmol dm^{-3}---		------mmol-----	
A	1	0.021	10.08	0.000	0.791
A	2	0.016	10.24	0.000	0.732
A	3	0.015	10.03	0.000	0.837
B	1	0.003	9.889	0.114	0.407
B	2	0.000	10.12	0.137	0.506
B	3	0.016	9.936	0.129	0.485
C	1	0.065	9.936	0.234	0.376
C	2	0.041	9.843	0.212	0.327
C	3	0.047	9.982	0.237	0.370
D	1	0.133	9.936	0.321	0.234
D	2	0.154	9.750	0.278	0.237
D	3	0.139	9.982	ND	ND
E	1	0.285	10.01	0.345	0.138
E	2	0.266	9.811	0.339	0.153
E	3	0.304	9.962	0.337	0.108
F	1	1.148	9.261	0.351	0.064
F	2	0.636	9.311	0.362	0.070
F	3	0.650	9.460	0.335	0.053
G	1	0.887	8.764	0.337	0.034
G	2	0.889	8.764	0.358	0.035
G	3	0.901	8.764	0.338	0.052
H	1	1.949	6.932	0.411	0.026
H	2	1.948	6.764	0.384	0.031
H	3	1.943	6.731	0.301	0.015
I	1	3.215	3.748	0.349	0.003
I	2	3.270	3.816	0.334	0.009
I	3	3.300	3.748	0.344	0.012
J	1	4.546	3.475	0.207	ND
J	2	4.517	3.398	0.392	0.000
J	3	4.595	3.411	0.379	ND
K	1	4.947	0.000	0.362	0.003
K	2	4.828	0.000	0.343	0.004

Table 9. Experimental exchange data for Set Seven.

Equilibration	Replication	Supernatant cation concentration		Exchangable cation content	
		Mg	Na	Mg	Na
		----mmol dm^{-3}---		------mmol-----	
A	1	0.000	9.991	0.000	0.812
A	2	0.000	10.04	0.000	0.866
A	3	0.000	9.941	0.000	0.885
B	1	0.019	10.09	0.042	0.736
B	2	0.016	10.14	0.043	0.720
B	3	0.017	10.14	0.044	0.706
C	1	0.053	9.941	0.048	0.632
C	2	0.076	9.741	0.051	0.994
C	3	0.071	9.642	0.048	0.629
D	1	0.110	9.891	0.152	0.432
D	2	0.103	9.691	0.162	0.450
D	3	0.103	9.791	0.165	0.506
E	1	0.040	9.941	0.120	0.542
E	2	0.043	9.941	0.135	0.532
E	3	0.037	9.841	0.129	0.572
F	1	0.261	9.448	0.266	0.282
F	2	0.252	9.345	0.264	0.283
F	3	0.274	9.396	0.243	0.283
G	1	0.483	9.139	0.304	0.197
G	2	0.396	9.191	0.301	0.227
G	3	0.402	9.139	0.303	0.234
H	1	1.726	6.804	0.351	0.084
H	2	1.722	6.597	0.363	0.086
H	3	1.737	6.597	0.334	0.075
I	1	3.191	3.709	0.389	0.041
I	2	3.137	3.815	0.389	0.042
I	3	3.164	3.744	0.381	0.043
J	1	4.355	1.128	0.342	0.011
J	2	4.400	1.115	0.351	0.012
J	3	4.355	1.117	0.348	0.011
K	1	4.917	0.000	0.358	0.004
K	2	4.850	0.000	0.343	0.005

Table 10. Mean supernatant solution cation concentration and exchangable cation mole fraction in ternary batch isotherm determinations with AG MP-50 macroporous cation resin.

Supernatant cation concentration			Exchangable cation content		
Ca	Mg	Na	Ca	Mg	Na
mmol dm^{-3}			mole fraction		
3.629 (±0.325)	0.992 (±0.002)	1.271 (±0.018)	0.945 (±0.011)	0.041 (±0.005)	0.014 (±0.011)
2.871 (±0.025)	0.759 (±0.003)	4.018 (±0.017)	0.911 (±0.008)	0.052 (±0.000)	0.037 (±0.007)
1.336 (±0.002)	0.389 (±0.002)	7.314 (±0.020)	0.887 (±0.033)	0.048 (±0.011)	0.065 (±0.022)
0.867 (±0.028)	0.194 (±0.008)	9.716 (±0.165)	0.794 (±0.055)	0.063 (±0.008)	0.144 (±0.049)
0.647 (±0.026)	0.125 (±0.003)	10.06 (±0.107)	0.747 (±0.034)	0.075 (±0.000)	0.178 (±0.034)
0.531 (±0.012)	0.120 (±0.002)	10.76 (±0.162)	0.680 (±0.008)	0.083 (±0.003)	0.237 (±0.005)
0.109 (±0.006)	0.065 (±0.003)	11.16 (±0.102)	0.494 (±0.009)	0.072 (±0.002)	0.434 (±0.009)
0.010 (±0.000)	0.003 (±0.000)	11.42 (±0.140)	0.163 (±0.006)	0.021 (±0.001)	0.816 (±0.006)
2.952 (±0.025)	1.927 (±0.024)	1.181 (±0.011)	0.859 (±0.004)	0.135 (±0.000)	0.006 (±0.003)
2.047 (±0.016)	1.388 (±0.007)	3.908 (±0.052)	0.849 (±0.003)	0.124 (±0.000)	0.027 (±0.003)
1.086 (±0.024)	1.043 (±0.000)	7.440 (±0.190)	0.779 (±0.022)	0.128 (±0.009)	0.094 (±0.031)
0.342 (±0.024)	0.391 (±0.025)	10.22 (±0.040)	0.595 (±0.011)	0.186 (±0.008)	0.219 (±0.019)
0.208 (±0.001)	0.306 (±0.007)	10.59 (±0.060)	0.454 (±0.048)	0.178 (±0.016)	0.368 (±0.064)
0.144 (±0.030)	0.201 (±0.017)	10.80 (±0.217)	0.422 (±0.003)	0.147 (±0.003)	0.431 (±0.012)
0.066 (±0.009)	0.177 (±0.026)	10.74 (±0.119)	0.277 (±0.096)	0.100 (±0.039)	0.623 (±0.135)
0.030 (±0.000)	0.016 (±0.001)	11.00 (±0.063)	0.089 (±0.012)	0.033 (±0.005)	0.878 (±0.017)

Table 10--continued.

Supernatant cation concentration			Exchangable cation content		
Ca	Mg	Na	Ca	Mg	Na
mmol dm^{-3}			mole fraction		
1.855 (±0.024)	2.916 (±0.045)	1.221 (±0.019)	0.762 (±0.030)	0.226 (±0.025)	0.012 (±0.004)
1.315 (±0.010)	2.012 (±0.073)	4.093 (±0.009)	0.751 (±0.023)	0.213 (±0.019)	0.036 (±0.004)
0.670 (±0.029)	1.231 (±0.039)	7.339 (±0.208)	0.678 (±0.010)	0.249 (±0.005)	0.073 (±0.005)
0.147 (±0.004)	0.218 (±0.013)	9.832 (±0.031)	0.462 (±0.017)	0.321 (±0.014)	0.216 (±0.003)
0.086 (±0.008)	0.235 (±0.016)	10.32 (±0.069)	0.362 (±0.015)	0.269 (±0.015)	0.369 (±0.029)
0.032 (±0.004)	0.137 (±0.008)	10.55 (±0.080)	0.312 (±0.014)	0.239 (±0.014)	0.449 (±0.029)
0.037 (±0.000)	0.040 (±0.004)	10.49 (±0.033)	0.236 (±0.003)	0.162 (±0.004)	0.602 (±0.006)
0.019 (±0.000)	0.023 (±0.000)	10.75 (±0.086)	0.091 (±0.002)	0.049 (±0.001)	0.860 (±0.002)
0.902 (±0.007)	3.592 (±0.138)	1.121 (±0.016)	0.565 (±0.005)	0.421 (±0.005)	0.014 (±0.000)
0.613 (±0.008)	2.832 (±0.073)	3.881 (±0.193)	0.547 (±0.003)	0.412 (±0.002)	0.042 (±0.001)
0.310 (±0.008)	1.473 (±0.059)	7.009 (±0.313)	0.503 (±0.014)	0.406 (±0.009)	0.091 (±0.006)
0.051 (±0.004)	0.399 (±0.050)	9.574 (±0.211)	0.261 (±0.017)	0.413 (±0.011)	0.325 (±0.029)
0.064 (±0.010)	0.244 (±0.049)	9.834 (±0.242)	0.228 (±0.020)	0.388 (±0.034)	0.384 (±0.054)
0.051 (±0.004)	0.185 (±0.012)	10.71 (±0.309)	0.220 (±0.013)	0.362 (±0.016)	0.418 (±0.025)
0.052 (±0.009)	0.138 (±0.016)	11.04 (±0.438)	0.147 (±0.007)	0.301 (±0.108)	0.551 (±0.109)
0.019 (±0.000)	0.039 (±0.002)	10.84 (±0.317)	0.027 (±0.007)	0.064 (±0.009)	0.909 (±0.002)

Table 11. Mean supernatant solution cation concentration and exchangeable cation mole fraction in binary batch isotherm determinations with AG MP-50 macroporous cation resin.

| Supernatant cation concentration | | | Exchangeable cation content | | |
| mmol dm⁻³ | | | mole fraction | | |
Ca	Mg	Na	Ca	Mg	Na
0.000 (±0.000)	5.067 (±0.034)		0.000 (±0.000)	1.000 (±0.000)	
0.169 (±0.006)	4.399 (±0.045)		0.352 (±0.003)	0.648 (±0.003)	
0.989 (±0.022)	4.115 (±0.026)		0.578 (±0.005)	0.422 (±0.005)	
1.466 (±0.012)	3.641 (±0.055)		0.688 (±0.013)	0.312 (±0.013)	
1.963 (±0.040)	3.183 (±0.021)		0.776 (±0.011)	0.224 (±0.011)	
0.000 (±0.000)	2.706 (±0.023)		0.868 (±0.008)	0.132 (±0.008)	
2.892 (±0.033)	2.115 (±0.030)		0.873 (±0.002)	0.127 (±0.002)	
3.371 (±0.045)	1.641 (±0.004)		0.911 (±0.003)	0.089 (±0.003)	
3.879 (±0.048)	1.150 (±0.034)		0.941 (±0.004)	0.059 (±0.004)	
4.229 (±0.097)	0.568 (±0.003)		0.990 (±0.003)	0.010 (±0.017)	
4.785 (±0.037)	0.000 (±0.000)		1.000 (±0.000)	0.000 (±0.000)	
0.017 (±0.003)		10.11 (±0.110)	0.000 (±0.000)		1.000 (±0.000)
0.006 (±0.008)		9.982 (±0.123)	0.214 (±0.004)		0.786 (±0.004)
0.051 (±0.006)		9.920 (±0.071)	0.389 (±0.005)		0.611 (±0.005)
0.142 (±0.011)		9.889 (±0.123)	0.559 (±0.028)		0.441 (±0.028)
0.285 (±0.010)		9.928 (±0.105)	0.720 (±0.034)		0.280 (±0.034)
0.811 (±0.292)		9.344 (±0.104)	0.849 (±0.013)		0.151 (±0.013)
0.892 (±0.007)		8.764 (±0.000)	0.895 (±0.025)		0.105 (±0.025)
1.947 (±0.003)		6.809 (±0.108)	0.939 (±0.013)		0.061 (±0.013)
3.262 (±0.043)		3.770 (±0.039)	0.976 (±0.013)		0.024 (±0.013)
4.553 (±0.039)		3.428 (±0.041)	1.020 (±0.019)		0.000 (±0.000)
4.888 (±0.084)		0.000 (±0.000)	0.990 (±0.003)		0.010 (±0.003)

Table 11--continued.

Supernatant cation concentration			Exchangable cation content		
Ca	Mg	Na	Ca	Mg	Na
mmol dm⁻³			mole fraction		
	0.000 (±0.000)	9.991 (±0.050)		0.000 (±0.000)	1.000 (±0.000)
	0.018 (±0.002)	10.12 (±0.029)		0.056 (±0.002)	0.944 (±0.002)
	0.067 (±0.012)	9.775 (±0.153)		0.063 (±0.013)	0.937 (±0.013)
	0.105 (±0.004)	9.791 (±0.100)		0.257 (±0.010)	0.743 (±0.010)
	0.040 (±0.003)	9.908 (±0.058)		0.189 (±0.011)	0.811 (±0.011)
	0.262 (±0.011)	9.396 (±0.051)		0.476 (±0.013)	0.524 (±0.013)
	0.427 (±0.048)	9.157 (±0.030)		0.581 (±0.024)	0.419 (±0.024)
	1.728 (±0.008)	6.666 (±0.120)		0.811 (±0.005)	0.189 (±0.005)
	3.164 (±0.027)	3.756 (±0.054)		0.902 (±0.004)	0.098 (±0.004)
	4.370 (±0.026)	1.120 (±0.007)		0.969 (±0.001)	0.031 (±0.001)
	4.884 (±0.048)	0.000 (±0.000)		0.987 (±0.003)	0.013 (±0.003)

Table 12. Binary exchange equilbria with montmorillonite reported by Elprince et al.(1980).

Cation solution concentration			Exchangable cation content		
La	Ba	NH$_4$	La	Ba	NH$_4$
---------mol dm^{-3}---------			---------- mmol----------		
0.00350	0.04455		0.1560	0.2595	
0.00524	0.04170		0.3987	0.4015	
0.00669	0.03945		0.6543	0.5255	
0.00783	0.03776		0.9253	0.6345	
0.00863	0.03665		1.2140	0.7340	
0.00175	0.03183		1.0560	0.4400	
0.01575	0.02573		0.8550	0.2280	
0.02075	0.01832		0.6073	0.0895	
0.02671	0.00959		0.3190	0.0220	
0.02618		0.01914	0.296		0.153
0.02074		0.03571	0.580		0.327
0.01599		0.05071	0.826		0.565
0.01191		0.06386	1.244		1.085
0.00859		0.07314	1.446		2.221
0.00764		0.07600	1.108		1.536
0.00641		0.07940	0.657		1.094
0.00503		0.08343	0.398		0.871
0.00307		0.08814	0.169		0.583
	0.04103	0.0814		9.05	1.9
	0.03391	0.03271		16.26	9.38
	0.02832	0.04443		21.96	16.08
	0.02425	0.05314		26.12	27.77
	0.02119	0.05886		29.24	42.3
	0.01868	0.06386		21.6	37.1
	0.01586	0.06900		14.3	31.7
	0.01249	0.07543		7.59	25.0
	0.00774	0.08457		2.29	15.68

Table 13. Ternary exchange equilbria with montmorillonite reported by Elprince et al.(1980).

Cation solution concentration			Exchangable cation content		
La	Ba	NH$_4$	La	Ba	NH$_4$
----------mol dm^{-3}---------			----------- mmol----------		
0.00138	0.04321	0.0096	0.1933	0.655	0.120
0.00181	0.03866	0.0171	0.4810	1.117	0.449
0.00200	0.03499	0.0237	0.7923	1.511	0.857
0.00216	0.03202	0.0294	1.1063	1.863	1.352
0.00302	0.02674	.0.0372	1.3500	1.407	1.547
0.00442	0.02283	0.0404	1.2083	0.755	1.149
0.00738	0.01708	0.0440	0.9120	0.307	0.716
0.01142	0.00940	0.0473	0.5107	0.063	0.319
0.00310	0.00884	0.0732	0.3523	0.1205	0.712
0.00298	0.01589	0.0591	0.6950	0.4295	1.185
0.00640	0.02367	0.0331	1.3471	0.6760	0.899
0.00770	0.03038	0.0158	1.8673	1.0400	0.747
0.00075	0.02219	0.0540	0.5873	1.8815	2.824
0.00299	0.02175	0.0475	1.0237	0.8720	1.424
0.01233	0.01775	0.0271	1.0753	0.2400	0.422
0.02033	0.00955	0.0194	0.6060	0.0485	0.127

data, least squares regressions were performed to fit the data to the following equation

$$\ln k^a_{(v)i/j} = \beta_0 + \beta_1 x_{j'} + \beta_2 x_{j'}^2 \qquad [51]$$

where $x_{j'}$ is the exchanger phase equivalent fraction of cation "j". The parameter estimates and coefficients of determination are presented in Tables 14 and 15. In one of the binary exchange experiments with montmorillonite, the parameter β_2 could be dropped from the regression of $\ln k^a_{(v)La/NH_4}$ on exchanger phase NH_4 equivalent fraction without decreasing the coefficient of determination. The thermodynamic exchange constants were calculated using the regression equations by evaluating the integral

$$\ln K_{exi/j} = \int_0^1 \ln k^a_{(v)i/j} \, dx_j^e \; .$$

that is

$$\ln K_{exi/j} = \beta_0 + \frac{\beta_1}{2} + \frac{\beta_2}{3}$$

The resulting estimated exchange constants were tested by the triangle rule

$$z_k \ln K_{exi/j} + z_i \ln K_{exj/k} + z_j \ln K_{exk/i} = 0.$$

Table 14. Quadradic model parameter estimates from least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on cation exchanger phase equivalent fraction in binary systems with AG MP-50 macroporous cation resin.

Dependant Variable	Parameter estimates			Coefficient of Determination (R^2)
	β_0 [†]	β_1	β_2	
ln $k^a_{(v)Ca/Mg}$	3.380	-2.732	8.593	0.941
ln $k^a_{(v)Mg/Na}$	-1.024	3.668	-4.739	0.533
ln $k^a_{(v)Na/Ca}$	-5.779	15.717	-12.171	0.960

[†]Parameter estimates for the model ln $k^a_{(v)i/j} = \beta_0 + \beta_1 x_j + \beta_2 x_j$, ^{2}.

Table 15. Quadradic model parameter estimates from least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on cation exchanger phase equivalent fraction in binary systems with montmorillonite.

Dependant Variable	Parameter estimates			Coefficient of Determination (R^2)
	β_0[†]	β_1	β_2	
ln $k_{(v)Ba/La}$	-1.654	-1.563	0.906	0.372
ln $k_{(v)La/NH4}$	-2.399	-2.072		0.326
ln $k_{(v)NH4/Ba}$	2.231	-3.092	2.765	0.491

[†]Parameter estimates for the model ln $k_{(v)i/j} = \beta_0 + \beta_1 x_{j'} + \beta_2 x_{j'}$[a], 2.

The parameters for each of the three quadratic regression parameters were adjusted so that the triangle rule was obeyed exactly. These adjusted parameter estimates are presented in Tables 16 and 17. The thermodynamic exchange constants and standard free energies of exchange for the cation resin and montmorillonite calculated using the adjusted regression parameters are presented in Table 18. The standard free energies of exchange measured in this study had higher absolute value than those reported by Boyd (1970). The difference was greatest for the Mg/Ca exchange reaction. These differences may be due to differences in electrolyte solution concentrations, methods of data analysis, or specific effects due to the common anion.

The regression equations and natural logarithms of the adjusted Vanselow selectivity coefficients determined in both the binary and ternary exchange experiments with the cation resin and with montmorillonite are plotted in Figures 4 through 9. These plots show that, at least qualitatively, that the relationships between $\ln k^a_{(v)i/j}$ and exchanger phase equivalent fractions were similar in both binary and ternary systems, though substantial deviations between the binary and ternary data were observed. The plot of $\ln k^a_{(v)Na/Ca}$ against exchanger phase equivalent fraction (Figure 4) determined in ternary experiments appeared to define a different curve than the $\ln k^a_{(v)Na/Ca}$ values determined in binary exchange experiments. There was so much scatter in the plots of

Table 16. Quadradic model parameter estimates from least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on cation exchanger phase equivalent fraction in binary systems with AG MP-50 macroporous cation resin adjusted so that calculated thermodynamic exchange constants adhere to the triangle rule.

Dependant Variable	Parameter estimates		
	β_0[†]	β_1	β_2
$\ln k_{(v)Ca/Mg}$	3.447	−2.665	8.660
$\ln k_{(v)Mg/Na}$	−0.957	3.735	−4.672
$\ln k_{(v)Na/Ca}$	−5.712	15.784	−12.104

[†]Parameter estimates for the model
$$\ln k_{(v)i/j}^{a} = \beta_0 + \beta_1 x_{j'} + \beta_2 x_{j'}{}^2.$$

Table 17. Quadradic model parameter estimates from least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on cation exchanger phase equivalent fraction in binary systems with montmorillonite adjusted so that calculated thermodynamic exchange constants adhere to the triangle rule.

Dependant Variable	Parameter estimates		
	β_0[†]	β_1	β_2
$\ln k_{(v)Ba/La}$	−2.269	0.048	0.910
$\ln k_{(v)La/NH4}$	−2.395	2.076	
$\ln k_{(v)NH4/Ba}$	2.235	−3.088	2.769

[†]Parameter estimates for the model
$$\ln k_{(v)i/j}^{a} = \beta_0 + \beta_1 x_{j'} + \beta_2 x_{j'}{}^2.$$

Table 18. Calculated thermodynamic exchange constants and standard free energies of exchange for AG MP-50 macroporous cation resin at 24.5° C and for montmorillonite at 25° C.

Exchanger	Exchange constant	Exchange constant value	Standard free energy of exchange
			--J mol^{-1}--
Cation resin			
	$Kex_{Na/Ca}$	0.157	4580
	$Kex_{Ca/Mg}$	148.641	-12400
	$Kex_{Mg/Na}$	0.524	1600
Montmorillonite			
	$Kex_{NH4/Ba}$	5.019	-4000
	$Kex_{Ba/La}$	0.119	5270
	$Kex_{La/NH4}$	0.258	3350
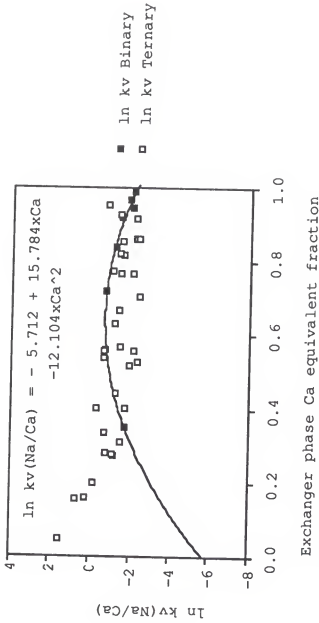
Figure 4. ln $k^a_{(V)Na/Ca}$ measured for Ca-Na (Binary) and Ca-Mg-Na (Ternary) exchange with AG MP-50 macroporous cation resin. The smooth line is a plot of the equation in the graph frame, which was determined by the least squares regression of ln $k^a_{(V)Na/Ca}$ on exchanger phase Na equivalent fraction in binary exchange experiments.
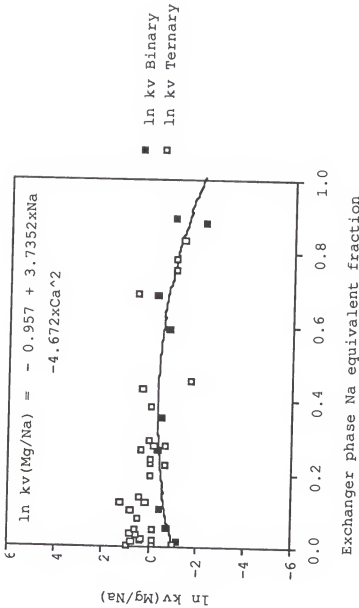
Figure 5. ln $k^a_{(V)Mg/Na}$ measured for Mg-Na (Binary) and Ca-Mg-Na (Ternary) exchange with AG MP-50 macroporous cation resin. The smooth line is a plot of the equation in the graph frame, which was determined by the least squares regression of ln $k^a_{(V)Mg/Na}$ on exchanger phase Na equivalent fraction in binary exchange experiments.
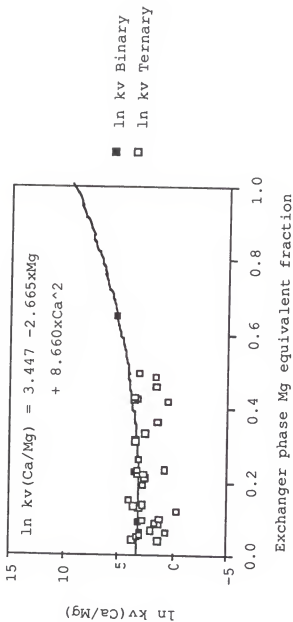
Figure 6. ln $k_{(V)Ca/Mg}^a$ measured for Ca-Mg (Binary) and Ca-Mg-Na (Ternary) exchange with AG MP-50 macroporous cation resin. The smooth line is a plot of the equation in the graph frame, which was determined by the least squares regression of ln $k_{(V)Ca/Mg}^a$ on exchanger phase Mg equivalent fraction in binary exchange experiments.
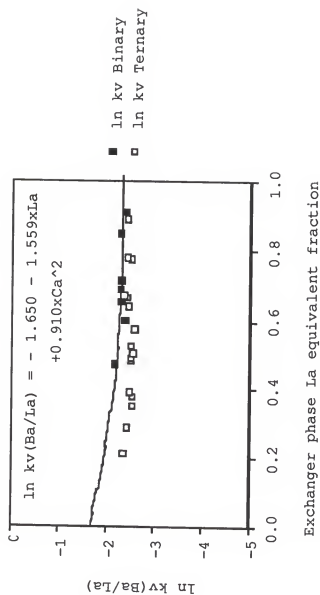
Figure 7. ln $k^a_{(V)Ba/La}$ measured for La-Ba (Binary) and La-Ba-NH$_4$ (Ternary) exchange with montmorillonite. The smooth line is a plot of the equation in the graph frame, which was determined by the least squares regression of ln $k^a_{(V)Ba/La}$ on exchanger phase Ba equivalent fraction in binary exchange experiments.
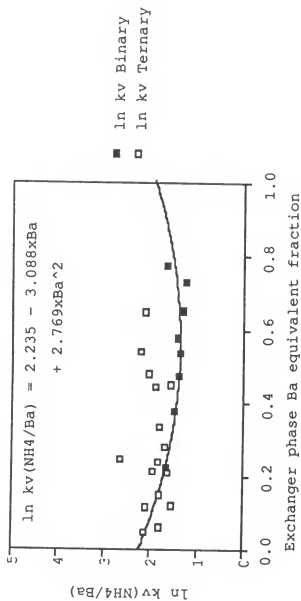
Figure 8. $\ln k^a_{(V)NH_4/Ba}$ measured for Ba-NH$_4$ (Binary) and La-Ba-NH$_4$ (Ternary) exchange with montmorillonite. The smooth line is a plot of the equation in the graph frame, which was determined by the least squares regression of $\ln k^a_{(V)NH_4/Ba}$ on exchanger phase Ba equivalent fraction in binary exchange experiments.
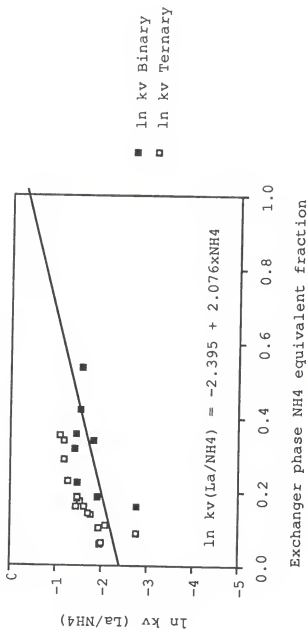
Figure 9. $\ln k^a_{(V)La/NH_4}$ measured for La-NH$_4$ (Binary) and La-Ba-NH$_4$ (Ternary) exchange with montmorillonite. The straight line is a plot of the equation in the graph frame, which was determined by the least squares regression of $k^a_{(V)La/NH_4}$ on exchanger phase NH$_4$ equivalent fraction in binary exchange experiments.

$\ln k^a_{(v)La/NH_4}$ against exchanger phase NH_4 equivalent fraction determined in both binary and ternary experiments that no clear relationship between $\ln k^a_{(v)La/NH_4}$ and exchanger phase NH_4 equivalent fraction was apparent, though a linear regression was used for the purposes of this study. In spite of these exceptions, the closeness of the plotted $\ln k^a_{(v)i/j}$ values against exchanger phase equivalent fraction determined in binary and ternary experiments suggests that relationships between $\ln k^a_{(v)i/j}$ and exchanger phase composition determined in binary exchange experiments could be valid frequently in predictions of ternary exchange equilibria.

The results of ternary experiments were analyzed similarly to the binary experiment results. Two possible regression models were evaluated, the simpler relation had four parameters

$$\ln k_{(v)i/j} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1 x_2, \qquad [52]$$

while the more intricate model

$$\ln k_{(v)i/j} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1^2 + \beta_4 x_1 x_2 + \beta_5 x_2^2 \qquad [53]$$

had six parameters. For both equations

x_1 = exchanger phase Na equivalent fraction, and

x_2 = exchanger phase Ca equivalent fraction,

for the resin exchange data; and

x_1 = exchanger phase NH_4 equivalent fraction, and

x_2 = exchanger phase Ba equivalent fraction

for the montmorillonite exchange data reported by Elprince et al. (1980).

If equations [52] and [53] are to be applied successfully to ternary exchange systems, the following relation must hold for all exchanger phase compositions

$$\frac{d(z_k \ln k_{(v)i/j} + z_i \ln k_{(v)j/k} + z_j \ln k_{(v)k/i})}{dx_i} = 0.$$

This criterion holds if

$$z_k \beta_n^{i/j} + z_i \beta_n^{j/k} + z_j \beta_n^{k/i} = 0, \text{ for } n = 1, 2, 3... \quad [54]$$

where $\beta_n^{i/j}$ is the n-th parameter in the regression equation [52] or [53], and $\beta_n^{j/k}$ and $\beta_n^{k/i}$ are the corresponding n-th parameters in the ternary-based regression equations having $\ln k_{(v)j/k}$ and $\ln k_{(v)k/i}$, respectively, as their dependant variables.

None of the regression parameter estimates deviated greatly from the relation expressed in equation [54] even though the restriction was not included in the calculation of the parameter estimates. Both models were used to estimate the exchanger phase composition. For both the cation resin and montmorillonite, the coefficient of determination was greater if the simpler regression model (Equation [52]) was used. As with the regression equations determined from binary

exchange data, the parameter estimates were adjusted to adhere to [54]. The adjusted parameter estimates for equation [52] for the cation exchanger are presented in Table 19 and for montmorillonite in Table 20. Since the parameter estimates were not calculated directly from least squares regression but adjusted to adhere to equation [54], the coefficients of determination from the original polynomial regressions are not presented.

Calculation of Exchanger Phase Activity Coefficient

The exchanger phase activity coefficients were estimated by evaluating the expressions

$$\ln f_i = \frac{1}{z_j} ((x^e_{i'} - 1)\ln k^a_{(v)i/j} + \int_{x^e_{i'}}^{1} \ln k^a_{(v)i/j} \, dx^e_{i'},), \qquad [26]$$

and,

$$\ln f_j = \frac{1}{z_i} (x^e_{i'} \ln k^a_{(v)i/j} - \int_{0}^{x^e_{i'}} \ln k^a_{(v)i/j} \, dx^e_{i'},) \qquad [27]$$

where $\ln k^a_{(v)i/j}$ was estimated by the quadratic regression equation calculated from the binary exchange data. Using the calculated exchanger phase activity coefficients, the exchanger phase activities could be estimated directly. For binary systems, these estimates could be compared to the

Table 19. Polynomial model parameter estimates from least
squares regressions of the natural logarithm of adjusted
Vanselow selectivity coefficients on cation exchanger phase
equivalent fractions in ternary systems with AG MP-50
macroporous cation resin.

Exchange selectivity	Parameter estimates			
	β_0 [†]	β_1	β_2	β_3
ln $k_{(v)Mg/Ca}$	-2.806	3.256	-0.236	-3.213
ln $k_{(v)Na/Mg}$	-0.725	2.135	0.533	-0.815
ln $k_{(v)Ca/Na}$	2.128	-3.763	-0.415	2.421

[†] Parameter estimates for the model
$k_{(v)i/j} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1 x_2$, where

x_1 = exchanger phase Ca equivalent fraction
x_2 = exchanger phase Na equivalent fraction.

Table 20. Polynomial model parameter estimates from least
squares regressions of the natural logarithm of adjusted
Vanselow selectivity coefficients on cation exchanger phase
equivalent fractions in ternary systems with montmorillonite.

Exchange selectivity	Parameter estimates			
	β_0 [†]	β_1	β_2	β_3
$k_{(v)Ba/NH4}$	-2.363	2.747	-0.024	-0.551
$k_{(v)La/Ba}$	2.372	0.477	0.207	-1.292
$k_{(v)NH4/La}$	2.359	-4.360	-0.067	1.473

[†] Parameter estimates for the model
$k_{(v)i/j} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1 x_2$, where

x_1 = exchanger phase NH_4 equivalent fraction
x_2 = exchanger phase Ba equivalent fraction

values assumed by the three exchanger phase reference functions considered in this study; the mole fraction, the equivalent fraction, and the statistical thermodynamic. Typical plots showing the relation between these reference functions and the calculated exchanger phase activity for Na on the cation resin and NH_4 on montmorillonite are presented in Figures 10 and 11, respectively. The closeness of the three reference functions to the calculated exchanger phase activity was examined by calculating the square root of the mean square error (RMSE) between the reference function and the calculated exchanger phase activity. The results of these calculations are presented in Table 21 for the cation resin and Table 22 for montmorillonite.

The RMSE statistic was used extensively in this study to compare the relative accuracy of predictions using chemical submodels to data from batch and column experiments. The use of statistics to validate and evaluate computer simulation models does not appear to be developed. Given the paucity of statistical techniques, its was decided to turn to regression analysis for guidance. In regression analysis, one method of validating a candidate regression model is to collect fresh data (that is data which has not been used in the calculation of the parameter estimates) and compare the R^2 for prediction ($R^2_{Prediction}$) with the coefficient of determination (R^2) for the original regression (Montgomery and Peck, 1982). The $R^2_{Prediction}$ is defined by

Table 21. The square root mean square error of between calculated exchanger phase activity and three reference functions for binary exchange on AG MP-50 macroporous cation resin.

		Reference function		
Cation predicted	System Considered	Mole fraction	Equivalent fraction	Statistical thermodynamic
		----Square root mean square error----		
Na	Ca-Na	0.083	0.204	0.026
Na	Mg-Na	0.037	0.086	0.104
Ca	Ca-Na	0.141	0.162	0.181
Ca	Ca-Mg	0.088		
Mg	Mg-Na	0.103	0.178	0.096
Mg	Ca-Mg	0.183		

Table 22. The square root mean square error between calculated exchanger phase activity and three reference functions for binary exchange on montmorillonite.

Cation predicted	System Considered	Reference function		
		Mole fraction	Equivalent fraction	Statistical thermodynamic
		----Square root mean square error----		
NH_4	Ba-NH_4	0.031	0.151	0.101
NH_4	La-NH_4	0.062	0.132	0.063
Ba	Ba-NH_4	0.020	0.138	0.089
Ba	La-Ba	0.001	0.074	0.053
La	La-NH_4	0.034	0.223	0.154
La	La-Ba	0.001	0.072	0.051

Table 23. Square root mean square error between measured exchanger phase mole fractions for binary and ternary exchange on AG MP-50 macroporous cation resin and exchanger phase mole fractions predicted by the use of three exchanger phase reference functions.

Cation predicted	System Considered	Reference function		
		Mole fraction	Equivalent fraction	Statistical thermodynamic
		----Square root mean square error----		
Na	Na-Ca-Mg	0.128	0.097	0.114
	Ca-Na	0.154	0.046	0.136
	Mg-Na	0.053	0.175	0.097
Ca	Na-Ca-Mg	0.207	0.113	0.192
	Ca-Na	0.154	0.048	0.137
	Ca-Mg	0.279	0.279	0.279
Mg	Na-Ca-Mg	0.136	0.151	0.138
	Mg-Na	0.053	0.183	0.097
	Ca-Mg	0.279	0.279	0.279

Table 24. Square root mean square error between measured exchanger phase mole fractions and exchanger phase mole fractions predicted by the use of three exchanger phase reference fucntions for binary and ternary exchange on montmorillonite.

		Reference function		
Cation predicted	System Considered	Mole fraction	Equivalent fraction	Statistical thermodynamic
		----Square root mean square error----		
NH_4	NH_4-Ba-La	0.008	0.034	0.030
	NH_4-La	0.109	0.161	0.137
	NH_4-Ba	0.139	0.230	0.151
Ba	NH_4-Ba-La	0.074	0.130	0.173
	NH_4-Ba	0.109	0.161	0.137
	Ba-La	0.142	0.145	0.381
La	NH_4-Ba-La	0.142	0.145	0.381
	Ba-La	0.068	0.144	0.149
	NH_4-La	0.139	0.230	0.151

Table 25. Square root mean square error between the measured exchanger phase mole fractions on AG MP-50 macroporous cation resin and exchanger phase mole fractions calculated by using polynomial multiple regression fits of the natural logarithm of adjusted Vanselow selectivity coefficients to exchanger phase equivalent fractions.

Cation predicted	Data used in regression	
	Binary	Ternary
	--Root mean square error--	
Na	0.080	0.066
Ca	0.079	0.065
Mg	0.063	0.054

Table 26. Square root mean square error between the measured exchanger phase mole fractions on montmorillonite and exchanger phase mole fractions calculated by using polynomial multiple regression fits of the natural logarithm of adjusted Vanselow selectivity coefficients to exchanger phase equivalent fractions.

	Data used in regression	
Cation predicted	Binary	Ternary
	--Root mean square error--	
NH_4	0.070	0.042
Ba	0.011	0.027
La	0.076	0.065
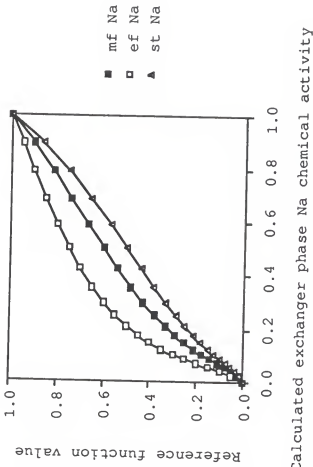
Figure 10. Relationship between calculated exchanger phase Na activities for Ca-Na exchange on AG MP-50 macroporous cation resin and the values taken by the Na mole fraction (mf), equivalent fraction (ef) and statistical thermodynamic (st) exchanger phase reference functions.
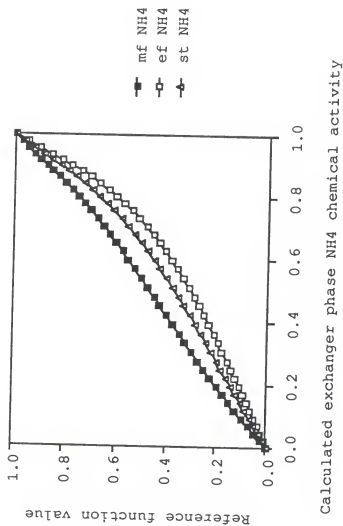
Figure 11. Relationship between calculated exchanger phase NH4 activities for Ba-NH4 exchange on montmorillonite and the values taken by the Ba mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.

$$R^2_{Prediction} = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \qquad [55]$$

where

y_i = the i-th observation of the dependant variable

$y\text{-hat}_i$ = the i-th predicted value of the dependant variable

$y\text{-bar}$ = the mean of all observed values of the dependant variable.

Since the total sum of squares, the denominator in equation [56], would be constant for all models evaluated with fresh data, the $R^2_{Prediction}$ measure would be inversely proportional to the mean square error (MSE or MS_E)

$$MSE = \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n} \qquad [56]$$

For qualitative comparisons, the square root of the mean square error (RSME) has an advantage over the MSE, because the RMSE measure has the same units as the dependant variable. Unlike the $R^2_{Prediction}$ measure, both the MSE and RMSE do not include information on the total variance of the dependant variable. It should be recalled that the total sum of squares from column studies, of the solute concentrations in the column effluent concentrations for example, would be much higher than the prediction error sum of squares (the

numerator in equation [55]), and calculated $R^2_{Prediction}$ could imply a unrealistic level of accuracy to the model under evaluation. All of the statistics, $R^2_{Prediction}$, MSE and RMSE are qualitative measures of predictive performance and statistically valid test of hypotheses cannot be calculated from them. Some may find them, however, superior to plots of measured and simulated data in conveying the accuracy of computer simulations.

No exchanger phase reference function was consistently closest to the exchanger phase activity in binary exchange on the cation exchanger, though the equivalent fraction failed to give the best estimate, as measured by RMSE, of any of the binary systems. For all of the binary exchange equilibria reported by Elprince et al. (1980), the mole fraction was consistently closer to the calculated exchanger phase activity and predictions due to the equivalent fraction reference function were consistently furthest. Therefore, for the two exchangers considered in this study, the mole fraction reference function consistently gave a close approximation of the exchanger phase activity. This result suggested that the mole fraction may be the preferred reference function in chemical submodels for cation transport models.

The ability of a reference function to approximate closely the exchanger phase activity for a wide range of compositions may be an important property for adherence of the corresponding defining relation to the thermodynamic

theory of ion exchange. Practically, and more importantly for this study, the preferred reference function should aid in the accurate calculation of the exchange equilibria. This ability was tested for the three reference functions and for least squares regression fits of the $\ln k^a_{(v)\,i/j}$ to exchanger phase equivalent fractions for binary and ternary exchange systems.

Evaluation of Exchanger Phase Reference Functions

Program BLCKBX was used to calculate the exchanger phase mole fractions for the cation resin and montmorillonite using the experimental supernatant solution compositions, the thermodynamic exchange constants and each of the three exchanger phase reference functions. Comparisons of predicted and measured exchanger phase compositions in ternary exchange are presented in Figures 12 through 17 for the cation resin and montmorillonite.

Several of the plots show that exchange information was not gathered in the for a full range of exchanger phase mole fractions. This is most notable for Mg on the cation resin (Figure 14) and for NH_4 on montmorillonite (Figure 17). With a limited number of equilibrations, it is difficult to select correctly the equilibrating solution compositions which will give exchange information for the range of exchanger phase compositions, especially for less competitive cations. Both NH_4 and Mg were the least preferred cations in their
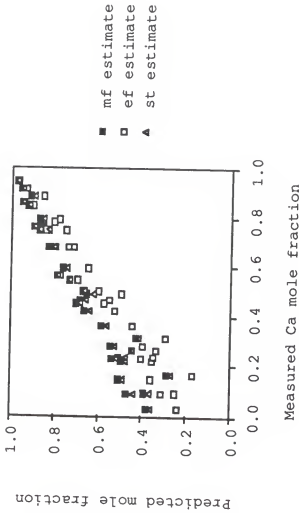
Figure 12. Measured Ca exchanger phase mole fractions for Na-Ca-Mg exchange on AG MP-50 macroporous cation resin and Ca exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.
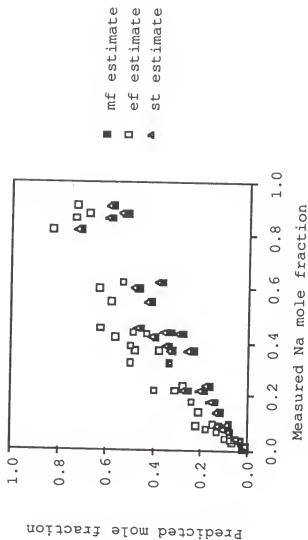
Figure 13. Measured Na exchanger phase mole fractions for Na-Ca-Mg exchange on AG MP-50 macroporous cation resin and Na exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.
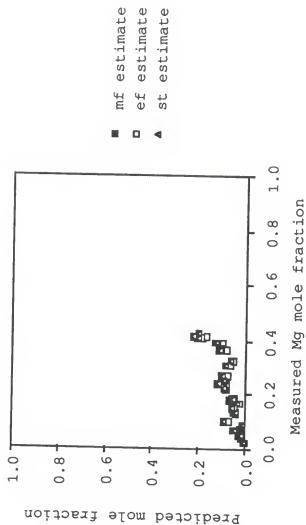
Figure 14. Measured Mg exchanger phase mole fractions for Na-Ca-Mg exchange on AG MP-50 macroporous cation resin and Mg exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.
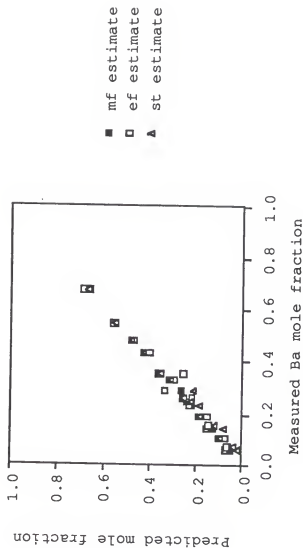
Figure 15. Measured Ba exchanger phase mole fractions for La-Ba-NH4 exchange on montmorillonite and Ba exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.
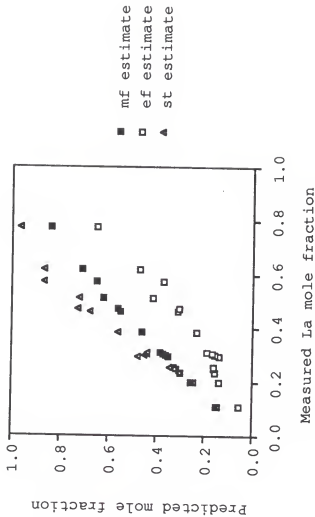
Figure 16. Measured La exchanger phase mole fractions for La-Ba-NH4 exchange on a cation resin and La exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.
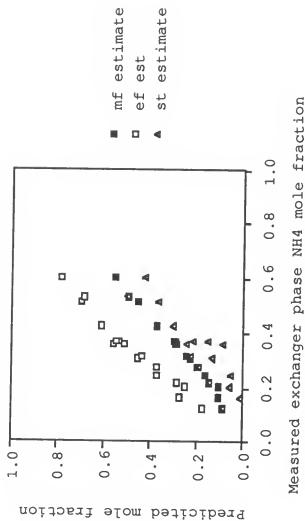
Figure 17. Measured NH4 exchanger phase mole fractions for La-Ba-NH4 exchange on montmorillonite and NH4 exchanger phase mole fractions predicted by using mole fraction (mf), equivalent fraction (ef), and statistical thermodynamic (st) exchanger phase reference functions.

respective ternary exchange experiments and it is not surprising that exchange data was lacking for higher exchanger phase mole fractions of these cations.

As before, the adequacies of various reference functions were evaluated by calculating the RMSE between predicted and measured exchanger phase mole fractions. Tables 23 and 25 show these RMSE values for the cation resin and montmorillonite, respectively. For ternary systems, the use of the equivalent fraction reference function appeared to give the closest estimate of Ca and Na mole fraction, while none of the RMSE values for predicted exchanger phase Mg mole fractions differed greatly.

In the binary exchange systems, the defining relations for the homovalent Ca-Mg system were identical and there were no difference between the predictions due to the three reference functions. The equivalent fraction reference function appeared to give the most accurate prediction of exchanger phase composition for Ca-Na systems, while use of the mole fraction reference function gave the best estimate in Mg-Na exchange systems.

The mole fraction reference function, which gave the best approximation of the calculated exchanger phase activity for exchange on montmorillonite reported by Elprince et al. (1980), also gave the most reliable prediction of exchanger phase composition in binary and ternary exchange experiments.

The exchanger reference function which yielded the most accurate prediction of exchanger phase composition was

different for the two experiments. For the data reported by Elprince et al. (1978), the use of the mole fraction exchanger phase reference function consistently gave more accurate estimates of exchanger phase compositions as indicted by lower RMSE between measured and predicted exchanger phase cation mole fractions. For exchange with synthetic exchange resins, the exchanger phase composition predictions using equivalent fraction reference function proved to be the most reliable, though differences among the predictions were not great. While it would be tempting to conclude that the different results between the two experiments were due to the nature of the exchangers, no conclusions could be drawn to the cause of the different predictive performance of the reference functions on the two ion exchangers because there were several differences between the two sets of experiments aside from exchanger type. Chloride salts were used by Elprince et al. (1978) while perchlorate salts were used in this study. The system studied by Elprince et al. (1978) consisted of cations with valences of 1+, 2+, and 3+, while the cations used in the present study had valences of 1+, 2+ and 2+. The equilibrating solutions used by Elprince et al. were maintained at constant chloride concentration of 0.1 mol dm^{-3}, while the equilibrating solutions in this study were maintained at a constant perchlorate concentration of 0.01 mol dm^{-3}. Although it may be suspected that the two exchanger phase reference function performed better on the different exchangers,

confounding factors eliminate the possibility of demonstrating conclusively this possibility. The prediction RMSE using the equivalent fraction reference function were smallest of the three when the differences between the three predictions were small. The differences between the predictions were greater when predicting the exchange equilibria of the data of Elprince et al. (1980). In that case, the predictions made using the mole fraction reference function yielded the smallest root mean square error. This trend was observed in evaluation of the predictions of cationic solute concentrations in the column effluent.

Regression equations derived from binary and ternary data were evaluated for their ability to predict the behavior of the ternary systems. The tabulation of the RMSE between measured exchanger phase mole fractions and those predicted by the use of variable selectivity coefficients for the cation resin and montmorillonite are presented in Tables 24 and 26, respectively. When compared to the best of suggested reference functions, the use of the binary-based regression equations reduced the root mean square error of the prediction by about half when the resin was the exchanger, but much less with the montmorillonite cation exchanger. With both exchangers, there appeared to be an improvement in the root mean square error of about 15% by using ternary-based regression equations instead of the binary-based regression equations. These results support, though weakly, the contention of Chu and Sposito (1980) that ternary exchange

data was needed to describe a ternary exchange system. It cannot be said if these improvements are "significant" because individuals, researchers, engineers, or planners would have to judge if the additional effort to determine these data will justify the expected increase in accuracy.

Regression equations which relate the logarithm of the adjusted Vanselow selectivity coefficient to the exchanger phase composition, the binary-based regression equations and ternary-based regression equations, have simple mathematical forms. The binary-based regression equations were degree two polynomials in the equivalent fraction of one of the two cations. The ternary-based regression equations were also degree two but only degree one in the equivalent fraction of either of the two cations which were independent variables. Attempts to include higher order terms in the regression analysis did not improve the coefficient of determination for these regression equations. The mathematical simplicity of the ternary-based regression equations suggests that their parameters could be estimated successfully by using binary-based regression equations.

Binary-based regression equations were used in this study calculate the exchanger phase activity coefficients for binary exchange using equations [26], [27], and [51]. In principle, regression equations derived from ternary data could be used to calculate exchanger phase activity coefficients for ternary systems. However, the derivation of these equations are beyond the scope of this study. Also

beyond the scope of this study, was an evaluation of the ability of the regression parameters derived from binary data to estimate the parameters of the ternary-based regression equations. If exchanger phase activity coefficients could be calculated for ternary systems as a function of the adjusted Vanselow selectivity coefficient and if the ternary-based regression coefficients could be estimated from binary data, then equations describing the exchanger phase activity coefficients in ternary systems could be derived accurately from binary data.

Column Experiments

The cation concentrations in the column effluent solutions are presented in Tables 27 and 28. As noted before, Run A consisted of a saturation of the column with 0.005 mol dm^{-3} $Ca(ClO_4)_2$ to which 61 cm^3 of a 0.0025 mol dm^{-3} $Mg(ClO_4)_2$, 0.005 mol dm^{-3} $NaClO_4$ solution was pumped. Run B consisted of a saturation of the column with 0.01 mol dm^{-3} $NaClO_4$ to which 61 cm^3 of a 0.0025 mol dm^{-3} $Mg(ClO_4)_2$, 0.0025 mol dm^{-3} $Ca(ClO_4)_2$ solution was pumped. The parameters used by program TABMODEL to simulate these column experiments are presented in Table 29.

Table 27. Measured column effluent mass and cation concentrations in Run A; which consisted of a pulse of a 0.05 mol dm^{-3} $NaClO_4$-0.025 mol dm^{-3} $Mg(ClO_4)_2$ solution introduced into a column saturated with a 0.05 mol dm^{-3} $Ca(ClO_4)_2$ solution.

Effluent fraction mass	Cation concentration		
	Na	Ca	Mg
--g--	--------mmol dm^{-3}--------		
9.96	0.000	5.198	0.264
10.19	0.000	5.198	0.264
9.98	0.000	5.198	0.264
10.26	0.000	5.198	0.264
10.12	0.117	5.087	0.242
10.33	0.199	5.144	0.231
10.01	0.953	4.705	0.242
9.72	2.956	4.023	0.264
10.58	4.794	2.971	0.308
10.12	4.928	2.545	0.424
10.34	5.410	2.445	0.667
10.23	5.113	2.057	0.893
10.27	4.799	1.846	1.214
10.06	3.362	1.933	1.854
10.29	0.807	2.118	2.705
10.17	0.068	2.022	3.069
10.04	0.085	2.145	3.025
10.45	0.000	3.015	2.157
9.90	0.000	5.006	0.759
10.19	0.035	5.089	0.281
10.53	0.017	5.351	0.225

Table 28. Measured column effluent mass and cation concentrations in Run B; which consisted of a pulse of a 0.25 mol dm^{-3} Ca(ClO$_4$)$_2$-0.025 mol dm^{-3} Mg(ClO$_4$)$_2$ solution introducted into a column saturated with a 0.10 mol dm^{-3} NaClO$_4$ solution.

Effluent fraction mass	Cation concentration		
	Na	Ca	Mg
--g--	--------mmol dm^{-3}--------		
10.00	10.491	0.103	0.331
9.85	10.491	0.103	0.331
9.90	10.491	0.103	0.331
9.72	10.491	0.103	0.331
9.55	10.518	0.342	0.456
10.09	10.917	0.147	0.395
9.59	10.892	0.103	0.341
10.19	10.518	0.094	0.341
10.19	9.214	0.796	0.893
9.97	6.697	1.321	1.427
9.83	4.266	2.009	2.014
9.53	1.293	2.636	2.583
9.76	0.647	3.095	2.690
9.61	2.530	2.561	1.836
10.15	7.233	1.704	1.195
9.97	9.394	0.769	0.688
9.88	11.164	0.342	0.537
9.87	10.261	0.339	0.555
9.89	10.316	0.408	0.608
9.90	9.756	0.526	0.715
10.20	10.343	0.185	0.448

Table 29. Parameters used in column experiment simulations.

		Column experiment	
Simulation parameter	Parameter units	Run A	Run B
Bulk density	kg dm^{-3}	1.48	1.48
Dispersion coefficient	cm^2 s	0.009023	0.009023
Cation exchange capacity	mol(+) kg^{-1}	0.004494	0.004494
Flow rate	mm s^{-1}	0.0419	0.0419
Length	dm	5.00	5.00
Area	dm^2	0.039761	0.039761
Water content	dm^3 dm^{-3}	0.32	0.32
Initial Na solution concentration	mol dm^{-3}	0.00	0.01
Initial Ca solution concentration	mol dm^{-3}	0.005215	0.00
Initial Mg solution concentration	mol dm^{-3}	0.00	0.00
Initial Na exchanger molality	mol kg^{-1}	0.00	0.004494
Initial Ca exchanger molality	mol kg^{-1}	0.002247	0.00
Initial Mg exchanger molality	mol kg^{-1}	0.00	0.00
Time of Pulse initiation	s	0.00	0.00
Pulse Na solution concentration	mol dm^{-3}	0.00569	0.00
Pulse Ca solution concentration	mol dm^{-3}	0.00	0.0025
Pulse Mg solution concentration	mol dm^{-3}	0.00249	0.0025
Time of Pulse termination	s	3660.0	3660.0

Comparison of Tabular Look-up and Valocchi Approaches

Two criteria were used to evaluate the ability of the tabular look-up and Valocchi approaches to predict the one-dimensional transport of three cations through porous media. The first criterion was the closeness the predicted first moments of cation concentration were to those of the experimental data. The first moment is mean time (measured in pore volumes) a solute pulse remains in the column. The first moment is defined by

$$\mu'_1 = \frac{\int Vc \, dV}{\int c \, dV} \tag{55}$$

where c is the solution concentration in the column effluent and V is the pore volume value (Villermaux,1981). The second criterion was the RSME between measured and predicted cation solution concentrations in the column effluent.

The measured column effluent data for Run A are presented in Figure 18 along with the predictions of an adaption of the Valocchi approach and predictions using the tabular look-up method with the equivalent fraction exchanger phase reference function. As shown in Table 18, the thermodynamic exchange constants indicate that Ca is
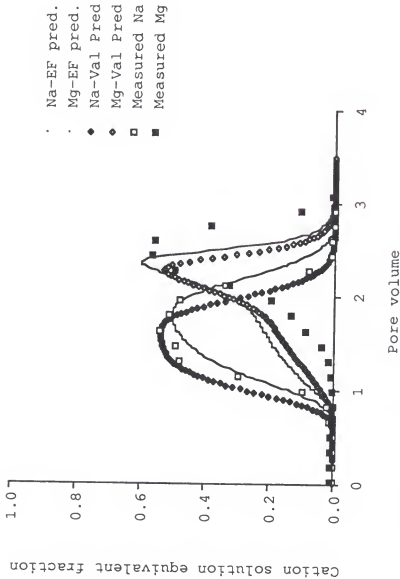
Figure 18. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg equivalent fractions predicted by the use of Valocchi approach to simulating cation transport through porous media and those predicted using the tabular look-up approach with equivalent fraction exchanger phase reference function (e.f. pred).

preferred by the resin over Na and that Ca is strongly preferred by the resin over Mg. The value calculated for $Kex_{Mg/Na}$ was 0.524, indicting a preference by the cation resin for Na over Mg. The measured Na peak was approximately symmetric, while the Mg concentration in the column effluent had the shape of a leading peak, an indication of a concave sorption isotherm faced by the solute in contact with the porous medium (Schweich and Sardin, 1981). These general peak shapes were duplicated successfully by each of the modeling approaches.

The solute pulse first moments for the measured data and the two simulations are presented in Table 30. Presented in Table 31 are root mean square error between the measured data and the simulations using the Valocchi and tabular look-up methods. As can be seen in Figure 18, there were small differences between the two predictions, though the results of the tabular look-up approach gave more accurate predictions of the distribution of cation concentrations in the effluent as measured by RMSE than did the Valocchi approach.

The calculation of exchange equilibria in the Valocchi approach of describing cation transport through porous media differs operationally from the tabular look-up approach. In the Valocchi approach, the concentrations of cations in solution determine the exchanger phase cation molality, while the tabular look-up approach uses the total amount of cations in both solution and exchanger phases to estimate the

Table 30. The first moments of the measured column effluent cation solution concentrations in Run A and those predicted using Valocchi and tabular look-up approaches in the development of cation transport models.

Cation in column effluent	Experimental	Simulation approach used		
		Valocchi	Tabular look-up	
			Exchanger phase reference function used	
		Mole fraction	Mole fraction	Equivalent fraction
		—Cation concentration first moment (Pore volumes) —		
Na	1.633	1.515	1.589	1.693
Ca	1.576	1.782	1.641	1.619
Mg	2.338	2.009	2.022	2.016

Table 31. Square root mean square error between the measured column effluent solution cation equivalent fraction and those predicted using Valocchi and tabular look-up approaches in the development of cation transport models.

Cation in column effluent	Simulation approach used		
	Valocchi	Tabular look-up	
		Exchanger phase reference function used	
		Mole fraction	Equivalent fraction
	-RMSE[†] (Solution equivalent fraction)-		
Na	0.038	0.045	0.073
Ca	0.157	0.138	0.187
Mg	0.143	0.132	0.151

[†]Square root mean square error.

Figure 19. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction exchanger phase reference function (m.f. pred).

Figure 20. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction (m.f. pred.) and statistical thermodynamic (s.t. pred.) exchanger phase reference functions.
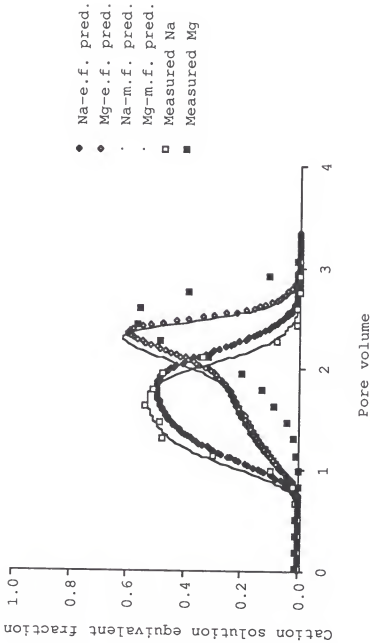
Figure 21. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction (m.f. pred) and equivalent fraction (e.f. pred) exchanger phase reference functions.

equilibrium distribution of the cations between the two phases. The latter approach has greater conceptual appeal, but judging from the results of these column simulations, the predictive improvement in abandoning the Valocchi method for the tabular look-up approach, while real, was modest. Further experiments with exchangers with different selectivities and different experimental initial and boundary conditions from the present study would be needed to determine the practical implications of these differences in operational computation of cation exchange.

Evaluation of Exchanger Phase Reference Functions

One objective of this study was to determine which of several exchanger phase reference functions provided the most accurate description of multicomponent cationic solute movement in porous media when used in a numerical solute transport model. As was discussed earlier, reference functions and selectivities chosen for use in solute transport models assume, usually implicitly, that the corresponding reference functions approximate solute exchanger phase activity. From a practical viewpoint, however, the more important property of a particular exchanger phase reference function is the predictive accuracy obtained when it is incorporated in a solute transport model. If a specific exchanger phase reference function gives a more accurate estimate of the exchanger phase activity than other

reference functions, such an exchanger phase reference function would be expected to provide more reliable simulation results when used in a solute transport model.

Two sets of column data were used in the evaluation of the three exchanger phase reference functions used in this study. The first column data were those generated in Run A of this study. The second were those presented by Lai et al. (1978) for a column packed with Yolo loam soil. While they used a column packed with soil rather than a quartz sand-cation resin mixture, the experimental boundary and initial conditions investigated by Lai et al. (1978) were similar to Run A. Lai et al. (1978) equilibrated their soil column packing to 0.125 mol $Ca(CH_3COO)_2$ dm^{-3} solution and introduced a 0.55 pore volume pulse of a 0.0625 mol $MgCl_2$-0.125 mol NaCl dm^{-3} solution.

The measured Run A effluent data and those predicted by the use of the mole fraction reference function are presented in Figure 19. These data are presented again with the prediction using the statistical thermodynamic the equivalent fraction reference function in Figure 20 and with the prediction using the equivalent fraction reference function in Figure 21. The differences between the effluent predictions and the predictions, as measured by the root mean squared error, are presented in Table 32. While differences among the predictions were not great, the statistical thermodynamic reference function gave the most accurate predictions for Na and Ca concentrations in the

Table 32. The first moment of the experimental column effluent cation solution concentrations and those predicted using three exchanger phase reference functions and polynomial least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on exchanger phase equivalent fractions.

Cation in column effluent	Experimental	Exchanger phase reference function used with fixed exchange selectivity			Exchange data used for regression	
		Mole fraction	Equivalent fraction	Statistical thermodynamic	Binary	Ternary
	------------------------------Cation concentration first moment (Pore volumes)------------------------------					
Na	1.633	1.589	1.693	1.604	1.572	1.577
Ca	1.576	1.641	1.619	1.637	1.579	1.550
Mg	2.338	2.022	2.016	2.025	2.392	2.535

Table 33. Square root mean square error between the measured column effluent solution cation equivalent fractions and those predicted using three exchanger phase reference functions and polynomial least squares regressions of the natural logarithm of adjusted Vanselow selectivity coefficients on exchanger phase equivalent fractions.

Cation in column effluent	Exchanger phase reference function used with fixed exchange selectivity			Exchange data used for regression	
	Mole fraction	Equivalent fraction	Statistical thermodynamic	Binary	Ternary
	----------RMSE[†] (Solution equivalent fraction)----------				
Na	0.038	0.045	0.032	0.042	0.040
Ca	0.157	0.138	0.150	0.100	0.123
Mg	0.143	0.132	0.138	0.065	0.091

[†]Square root mean square error.

Table 34. Calculated effluent cation solution mass-balance errors for five implementations of tabular look-up approach to the simulation of Case A.

Implementation type	Total mass-balance error	Proportion of total error for each cation		
			Cation	
		Na	Ca	Mg
	-percent-	--percent of total--		
Mole fraction	7.36	7.25	3.20	89.55
Equivalent fraction	1.13	19.26	1.82	78.93
Statistical thermodynamic	1.02	3.37	1.43	95.20
Binary regression	7.73	6.58	3.35	90.07
Ternary regression	0.78	1.79	9.06	89.15

Figure 22. Solution Na and Mg equivalent fractions measured in column effluent reported by Lai et al. (1978) and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction reference phase reference function (m.f. pred).

134
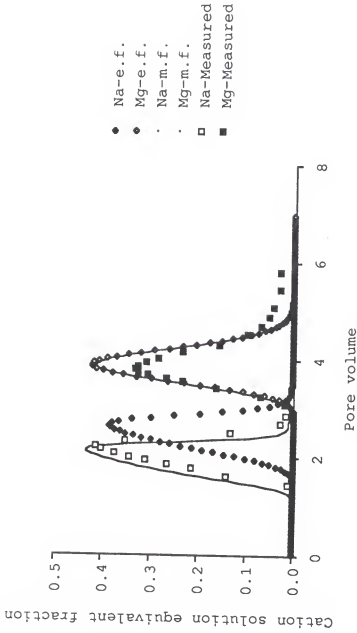
Figure 23. Solution Na and Mg equivalent fractions measured in column effluent reported by Lai et al. (1978) and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction (m.f. pred) and equivalent fraction (e.f. pred) exchanger phase reference functions.
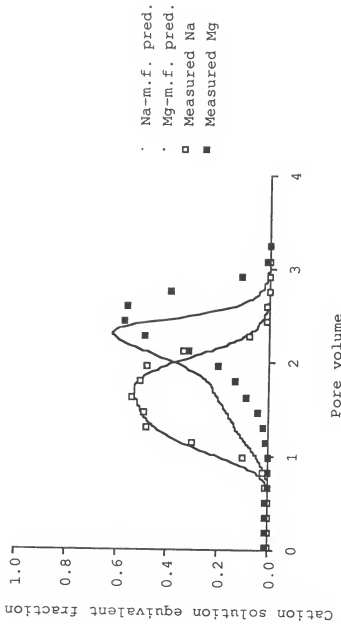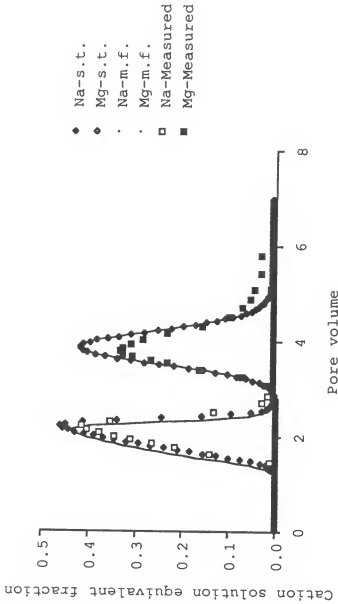
Figure 24. Solution Na and Mg equivalent fractions measured in column effluent reported by Lai et al. (1978) and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with mole fraction (m.f. pred.) and statistical thermodynamic (s.t. pred.) exchanger phase reference functions.
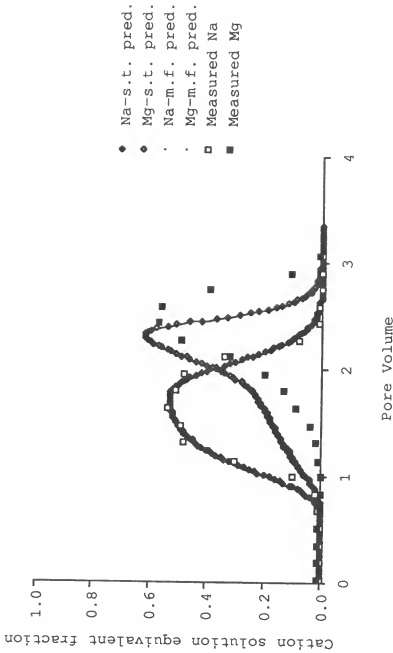
columneffluent while the equivalent fraction reference function gave the most accurate predictions for Mg concentrations in the column effluent. The measured and predicted concentration first moments are presented in Table 33. None of the reference functions gave a superior prediction of the first moment of the cation concentration in the column effluent. The mass-balance errors in the computer simulations based on the various tested models are presented in Table 34.

The measured effluent data presented by Lai et al. (1978) and those predicted by the use of the mole fraction reference function are presented in Figure 22. The Na peak has a slight leading shape, indicating that Na was less preferred by the soil than the other two cations, while the Mg peak had a trailing shape indicating that Mg was preferred by the soil over its counterions in the system. The column effluent data are presented again with the prediction using the equivalent fraction reference function in Figure 23 and with the prediction using the statistical thermodynamic reference function in Figure 24. While the predictions using the mole fraction and equivalent fraction reference functions were roughly equivalent and closely match the measured data, the equivalent fraction predictions were different from the others and predicted the column response much more poorly that those of the other two reference functions. This difference in predictive ability was most noticeable for the Na peak. Unlike the data developed from the cation resin used

in this study, the Na and Mg peaks presented by Lai et al. (1978) for soil appeared to have separated chromatographically soon after being introduced into thecolumn. Since the Na peak represents essentially a binary heterovalent system, it is suggested that the equivalent fraction reference function may be less accurate for predicting the transport of cations in binary heterovalent systems.

In simulations of the column effluent data reported by Lai et al. (1978), the use of the mole fraction and statistical thermodynamic reference functions gave excellent descriptions of their data. The use of the equivalent fraction reference function resulted in substantial errors in effluent cation concentration predictions. As with the predictions of batch cation exchange equilibria, in some experimental conditions all three of the reference functions tested here predicted column effluent cation concentration distributions with equivalent accuracy. In other conditions, however, the mole fraction was superior to the equivalent fraction reference function. It is suggested, therefore, that while the mole fraction reference function did not always give the most accurate predictions of exchange equilibria, it appeared to be the more reliable by not giving large errors under certain conditions. The use of the mole fraction exchanger phase reference function failed to be the most accurate in situations where modest differences existed between predictions made by using the various exchanger phase

reference functions. In those cases where substantial differences existed, the mole fraction was superior in the cases evaluated by this study. An exception to this observation is in the column effluent data of Lai et al. (1978), where predictions using the statistical thermodynamic reference function were roughly as accurate as those using the mole fraction reference function.

Effect of Variable Selectivity Coefficients on Predicted Column Response

All solute transport models, indeed all mathematical models, have some error in their predictions; models of solute cations in heterovalent, multicomponent systems require complex chemical submodels and may have more error than solute transport models describing systems with more simpler adsorption behavior. A problem addressed in this study was the degree to which improvements in the chemical submodel should improve overall model predictions of solute transport. For example, assume that by using variable rather than fixed exchange selectivities as input parameters in the model, the error in the predictions of batch exchange equilibria was decreased by 50%. One would not necessarily know, however, if this improvement in accuracy would be duplicated if variable exchange selectivities replaced fixed exchange values in a cation transport model.

To this end, regression equations which related the natural logarithm of the adjusted Vanselow selectivity coefficient to exchanger phase composition were used to predict the exchanger phase composition determined in the batch experiments. Two sets of regression equations were calculated; one set was based on binary exchange data while the second set was based on the results of ternary exchange experiments. These sets of equations were referred to as the "binary-based regression equations" and the "ternary-based regression equations", respectively. Chu and Sposito (1980) argued forcefully that ternary ion exchange data were necessary to accurately describe ternary exchange equilibria. Increased accuracy of these two types of regression equations in both batch and solute transport systems should indicate the predictive advantage from the use of ternary exchange data.

The measured effluent data from Run A, those predicted by the use of the mole fraction reference function with constant selectivity coefficients, and those predicted by using binary-based regression equations are presented in Figure 25. The measured effluent data, those predicted by the use of the mole fraction reference function with constant selectivity coefficients, and those predicted by selectivity coefficients predicted by regression equations obtained by fits to ternary data are presented in Figure 26. The predictions due to binary and ternary regressions are presented in Figure 27. The RMSE of these predictions are
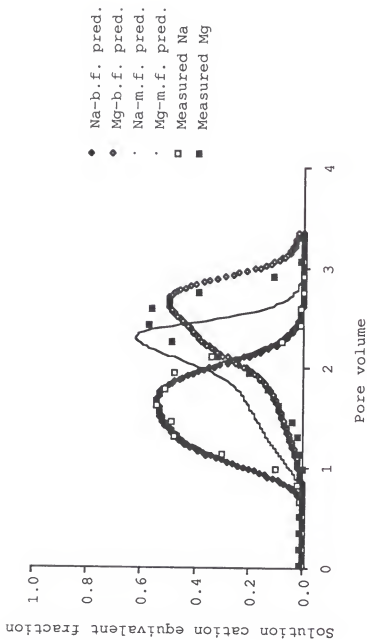
Figure 25. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg solution equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with fixed (m.f. pred) and variable (b.f. pred) Vanselow exchange selectivities. The regression parameters used to calculate the variable Vanselow exchange selectivities were derived from binary exchange experiments.

Pore volume
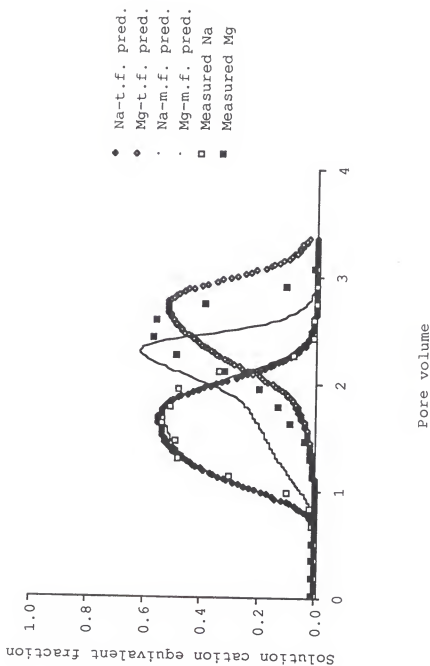
Figure 26. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media with fixed (m.f. pred) and variable (t.f. pred) Vanselow exchange selectivities. The regression parameters used to calculate the variable Vanselow exchange selectivities were derived from ternary exchange experiments.
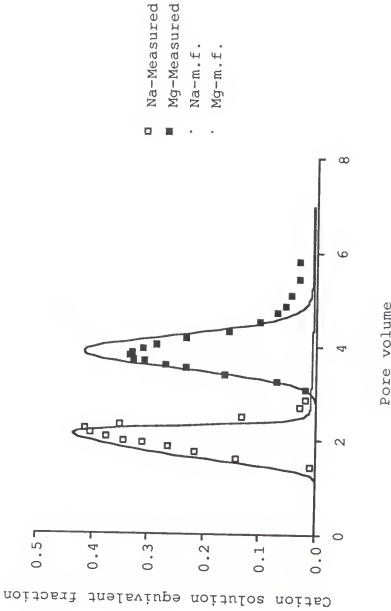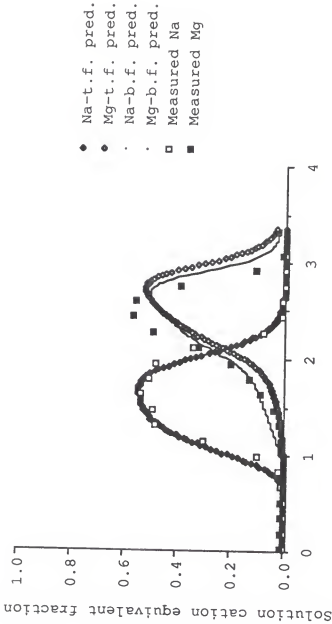
Figure 27. Solution Na and Mg equivalent fractions measured in column effluent sampled during Run A and solution Na and Mg solution equivalent fractions predicted by the use of tabular look-up approach to simulating cation transport through porous media variable (b.f. pred) Vanselow exchange selectivities. The regression parameters used to calculate the variable Vanselow exchange selectivities were derived from binary (b.f.pred)and ternary (t.f. pred) exchange experiments.

presented in Table 32, and the cation column effluent concentration distribution first moments are presented in Table 33. Predictions of column effluent cationic solute concentrations were improved by as much as half by using binary-based regression equations. No improvement was found by using ternary-based regression equations. The predictions using these regression equations were, if anything, worse than those using binary-based regression equations. This result suggested that while there was an improvement in the prediction of ternary batch exchange equilibria by using ternary exchange data, there was no similar improvement in the prediction of solute transport by incorporating the ternary-based regression equations in chemical submodels of solute transport models.

Suggested Future Research

Results of this study suggest several avenues for further research. First, under some experimental conditions the use of the mole fraction exchanger phase reference function gave predictions superior to the other tested reference functions. This study, however, did not clarify under what specific conditions the predictions following from the various reference functions will give similar predictions of exchange equilibria and under what conditions they will give significantly different predictions in batch and column experiments.

Second, ternary exchange information in this work conveyed little predictive improvement to ternary batch and no improvement to predictions of a column experiment. Further research should address the possibility that binary exchange data is adequate for the description of quaternary and higher order multication systems.

Third, the use of thermodynamic description of ion exchange reactions as chemical submodels in solute transport models assumed implicitly that the kinetics of the exchange process did not affect significantly the transport of the cations. Kinetic effects should be most noticeable at high interstitial velocities as were used in these column experiments. This study has shown that accurate descriptions of column response could be made using only the thermodynamic description of cation exchange, even at flow rates greater than typically imposed on soil column studies. Still, this study has not shown if the model predictions could be improved by including kinetic effects in the chemical submodel. Resolution of this possibility is needed in future experiments.

Note: The current recommendations of the International Union of Pure and Applied Chemistry (IUPAC) was used as the guide for the symbols and nomenclature used in this dissertation (MacGlashen, 1979; Irving, 1972). The only major deviations from the IUPAC recommendations is the use of the apostrophe after a subscript to indicate that the unit of measurement is on an equivalent basis (e.g. c_i^s and $c_{i'}^s$, are the solution concentrations of "i" in

units of mol dm^{-3} and $\frac{1}{z_i}$ mol dm^{-3}, respectively), the use of the superscript "e" to refer to the exchanger (solid) phase, and the use of the superscript "s" to refer to the solution (liquid) phase.

a_i^e = activity of solute i in the exchanger phase

a_i^s = activity of solute i in the solution phase

C = cation exchange capacity of the porous medium (mol(+) kg^{-1})

c_i^s = ion i solution concentration (mol dm^{-3})

$c_{i'}^s$ = ion i solution equivalent concentration ($\frac{1}{z_i}$ mol dm^{-3})

$c_{\Sigma+}^s$ = sum of the charge born by all cations in solution (mol(+) dm^{-3})

D = Coefficient of longitudinal dispersion (dm^2 s^{-1})

D_i = Denominator appropriate for an exchanger phase reference function

d_i = distribution coefficient (dm^3 kg^{-1})

$$d_i = \frac{m_i^e}{c_i^s}$$

e = Superscript designating the exchanger phase

feq(i) = equivalence factor of cation i

f_i = exchanger phase activity coefficient

g = Gas phase

i = a designation for cation i

I_c = ionic strength of the electrolyte solution (concentration basis)

j = a designation for cation j

$k_{(RJ)i/j}$ = Rubin-James selectivity coefficient

$k_{(V)i/j}$ = Vanselow selectivity coefficient

$k_{(VAL)i/j}$ = Valocchi selectivity coefficient

$k_{(GT)i/j}^a$ = adjusted Gaines-Thomas selectivity coefficient

$k_{(ST)i/j}^a$ = adjusted Statistical Thermodynamic selectivity coefficient

$k_{(V)i/j}^a$ = adjusted Vanselow selectivity coefficient

$k_{i/j}^a$ = an adjusted exchange selectiviy coefficient

K_{cj} = concentration equilibrium constant for the production of derived species j

K_d = linear partition coefficient

$K_{exi/j}$ = thermodynamic exchange constant

$k_{i/j}$ = an exchange selectivity coefficient

L   = differential operator

$$L = D \frac{\delta^2}{\delta t^2} - u \frac{\delta}{\delta z}$$

L_e^0 = zero-order rate coefficient of production in solid(s^{-1})

L_s^0 = zero-order rate coefficient of production in solution (mol dm^{-3} s^{-1})

L_e^1 = first-order rate coefficient of decay in solid (s^{-1})

L_s^1 = first-order rate coefficient of decay in solution (s^{-1})

m_i^e = exchanger phase concentration, mol kg^{-1}

$m_{i'}^e$ = ion i solid solution equivalent molality ($\frac{1}{z_i}$ mol kg^{-1})

n   = number of cations in the exchange system

n_i^e = number of moles of i in the solid phase

n_w^e = number of moles of i in the liquid phase

$$n_{w'}^e = \frac{n_w^e}{z_i n_i^e + z_j n_j^e}$$

N_i = $\rho_b m_i^e + \theta c_i^s$

N_i = total concentration of cation i in exchanger and solution phases (mol dm^{-3})

n_i^s = number of moles of solute i in the solution phase

R $\quad$ = molar gas constant $(J\ K^{-1}\ mol^{-1})$

$r(\zeta)$ $\quad$ = a reference function

r_i^e $\quad$ = exchanger phase reference function

r_i^s $\quad$ = solution phase reference function

s $\quad$ = Solution phase

T $\quad$ = temperature (K)

t $\quad$ = time (s)

u $\quad$ = interstitial velocity $(dm\ s^{-1})$

w $\quad$ = subscript for the solute

x_i^e $\quad$ = mole fraction of cation i in the exchanger phase

$x_{i'}^e$ $\quad$ = equivalent fraction of cation i in the exchanger phase

y_i $\quad$ = multiplicative factor suggested by Krishnamoorthy et al. (1948) equal to $(z_i + 1)/2$

z $\quad$ = length in the z direction (dm)

z_i $\quad$ = the absolute value of the valence of ion i

z_j $\quad$ = the absolute value of the valence of ion j

z_k $\quad$ = the absolute value of the valence of ion k

Δt $\quad$ = finite difference of time

Δx $\quad$ = finite difference of variable x

Δy $\quad$ = finite difference of variable y

Δz $\quad$ = finite difference of variable z

γ_i $\quad$ = solution phase activity coefficient

μ $\quad$ = chemical potential

μ_i^e = exchanger phase cation i chemical potential

μ_i^{eo} = standard state exchanger phase cation i chemical potential

μ_w^{eo} = standard state exchanger phase solvent chemical potential

μ_w^e = exchanger phase solvent chemical potential

μ_i^s = solution phase cation i chemical potential

μ_i^{so} = standard state solution phase cation i chemical potential

θ = volumetric water content (dm^3 dm^{-3})

ρ_b = porous medium bulk density (kg dm^{-3})

ζ^* = the reference state

```
      PROGRAM TBLMKR
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK, IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,   MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CHARACTER FINPUT*50,FOUTPT*50
      WRITE(*,*) 'INPUT FILE NAME'
      READ(*,140) FINPUT
      OPEN(UNIT=10,FILE=FINPUT,STATUS='OLD')
      WRITE(*,*) 'OUTPUT FILE NAME'
      READ(*,140) FOUTPT
      OPEN(UNIT=4,FILE=FOUTPT,STATUS='NEW')
C
C
C ********************************************************************
C
C
C
C
C        THE SUBROUTINES
C
C
C ********************************************************************
C
C
C
C
C BLCKBX = THIS SUBROUTINE CALCULATES THE PARTITIONING OF THREE CATIONS
C          BETWEEN THE EXCHANGER AND SOLUTION PHASES.
C
C CCALC  = USING THE PROPORTION OF CEC*BULKD AND THETA*TOTNOR, THIS
C          SUBROUTINE GIVES A FIRST ESTIMATE OF THE DISTRIBUTION OF
C          THREE IONS BETWEEN THE TWO PHASES
C
C DENOM  = CALCULATES THE DENOMINATOR OF THE REFERENCE FUNCTION CHOSEN
TO
C          APPROXIMATE THE EXCHANGER PHASE ACTIVITY.
C
C F      = CALCULATES THE EXCHANGER PHASE ACTIVITY COEFFICIENTS
C
C FCALC  = CALCULATES THE EXCHANGER PHASE MOLE FRACTION FOR EACH CATION
C
```

```
C GAMMA   = CALCULATES THE SOLUTION PHASE ACTIVITY COEFFICIENTS FOR
C           EACH CATION
C
C INPUT   = INPUTS PARAMETER FILE
C
C ITHENJ  = (ALSO ITHENK, JTHENI, JTHENK, KTHENI, KTHENJ) THESE
C           SUBROUTINES USE THE DEFINING RELATION OF THE VANSELOW
C           SELECTIVITY COEFFICIENT TO ESTIMATE ONE OF THE CATIONS
C           THE SECOND IS ESTIMATED BY DIFFERENCE (THE THIRD IS FIXED)
C           IF THE ESTIMATE OF THE SECOND ION IS NEGATIVE, THEN THE
C           ION CONCENTRATION VALUES REVERT TO THEIR PREVIOUS VALUES
C           AND ANOTHER SUBROUTINE IS TRIED. IF THE ESTIMATE OF THE
C           SECOND ION IS POSITIVE. THE TWO IONS ARE ESTIMATED
ITERATIVELY
C           UNTIL A CONVERGENT SOLUTION IS REACHED
C
C KCALC   = CALCULATES THE VANSELOW SELECTIVITY COEFFICIENT (ADJUSTED FOR
C           SOLUTION PHASE ACTIVITY COEFFICIENTS)
C
C OUTPUT  = OUTPUTS RESULTS, NOT CALLED IN CURRENT IMPLIMENTATION
C
C
C
C  *********************************************************************
C
C
C
C
C      THE VARIABLES
C
C
C
C  *********************************************************************
C
C
C
C
C      THE VARIABLES IN COMMON BLOCK STEVES
C
C BULKD   = THE BULK DENSITY (KG/DECIMETER^3)
C
C CBARI   = EXCHANGER PHASE CONCENTRATION (MOL/KG)
C
C CBARJ   = EXCHANGER PHASE CONCENTRATION (MOL/KG)
C
C CBARK   = EXCHANGER PHASE CONCENTRATION (MOL/KG)
C
C CCI     = THE TOTAL AMOUNT OF ION I IN THE SYSTEM (MOL/DECIMETER^3)
C
C CCJ     = THE TOTAL AMOUNT OF ION J IN THE SYSTEM (MOL/DECIMETER^3)
C
C CCK     = THE TOTAL AMOUNT OF ION K IN THE SYSTEM (MOL/DECIMETER^3)
C
C CCTN    = THE SUM OF ALL CATIONIC CHARGE IN THE SYSTEM
(MOL(+)/DECIMETER^3)
C
C CECFIX  = THE CATION EXCHANGE CAPACITY (MOL(+)/KG)
C
C CI      = SOLUTION PHASE CONCENTRATION (MOL/DECIMETER^3)
```

```
C
C CJ      = SOLUTION PHASE CONCENTRATION (MOL/DECIMETER^3)
C
C CK      = SOLUTION PHASE CONCENTRATION (MOL/DECIMETER^3)
C
C CTOTAL = THE TOTAL SOLUTION NORMALITY (MOL(+)/DECIMETER^3)
C
C FI      = THE EXCHANGER PHASE ACTIVITY COEFFICIENT FOR ION I
C (DIMENSIONLESS)
C
C FJ      = THE EXCHANGER PHASE ACTIVITY COEFFICIENT FOR ION J
C (DIMENSIONLESS)
C
C FK      = THE EXCHANGER PHASE ACTIVITY COEFFICIENT FOR ION K
C (DIMENSIONLESS)
C
C EPFRCI = THE ION I EXCHANGER PHASE MOLE FRACTION (DIMENSIONLESS)
C
C EPFRCJ = THE ION J EXCHANGER PHASE MOLE FRACTION (DIMENSIONLESS)
C
C EPFRCK = THE ION K EXCHANGER PHASE MOLE FRACTION (DIMENSIONLESS)
C
C EXPFRC = PROPORTION OF THE SYSTEM TOTAL CATIONIC CHARGE FOUND IN THE
C          EXCHANGER PHASE (DIMENSIONLESS)
C
C GAMMAI = THE SOLUTION PHASE ACTIVITY COEFFICIENT FOR ION I
C (DECIMETER^3/MOL)
C
C GAMMAJ = THE SOLUTION PHASE ACTIVITY COEFFICIENT FOR ION J
C (DECIMETER^3/MOL)
C
C GAMMAK = THE SOLUTION PHASE ACTIVITY COEFFICIENT FOR ION K
C (DECIMETER^3/MOL)
C
C IDEBUG = MARKER CONTROLLING DEBUGGING PRINTOUT
C               IDEBUG LT 1   NO DEBUGGING PRINTOUT
C               IDEBUG GE 1   DUBUGGING STATEMENTS WRITTEN
C
C IJ      = FLAG WHICH INDICTES IF THE BINARY EQUILIBRIUM
C           BETWEEN IONS I AND J (K FIXED) HAS BEEN SOLVED FOR
C           THE CURRENT ITERATION
C
C IJK     = COUNTER OF THE NUMBER OF BINARY EQUILIBRIA SOLVED FOR
C           THE CURRENT ITERATION. THE ITERATION IS COMPLETE WHEN
C           IJK EQUALS 2
C
C IRF     = MARKER INDICATING WHICH REFERENCE FUNCTION HAS BEEN
C           CHOSEN TO REPRESENT THE CATION EXCHANGER PHASE ACTIVITY
C
C           MOLE FRACTION = 1; EQUIVALENT FRACTION = 2;
C           STATISTICAL THERMODYNAMICAL = 3
C
C ISBMRK = MARKER INDICATING WHICH OF THE ATHENB IS
C          CALLING THE DENOM SUBROUTINE
C
C          ITHENJ = 1; ITHENK = 2; JTHENI = 3;
C          JTHENK = 4; KTHENI = 5; KTHENJ = 6
C
```

```
C ITRLIM = THE MAXIMUM NUMBER OF ITERATIONS ALLOWED IN ANY
C            SUBROUTINE OR THE MAIN PROGRAM
C
C JK     = FLAG WHICH INDICTES IF THE BINARY EQUILIBRIUM
C            BETWEEN IONS J AND K (I FIXED) HAS BEEN SOLVED FOR
C            THE CURRENT ITERATION
C
C KI     = FLAG WHICH INDICTES IF THE BINARY EQUILIBRIUM
C            BETWEEN IONS K AND I (J FIXED) HAS BEEN SOLVED FOR
C            THE CURRENT ITERATION
C
C RKIJ   = THE KVIJ VANSELOW SELECTIVITY COEFFICIENT ADJUSTED TO
C INCORPORATE
C            SOLUTION PHASE ACTIVITY COEFFICIENTS, (DIMENSIONLESS)
C
C RKIJ0  = THE THERMODYNAMIC EXCHANGE CONSTANT, KIJ (DIMENSIONLESS)
C
C RKJK   = THE KVJK VANSELOW SELECTIVITY COEFFICIENT ADJUSTED TO
C INCORPORATE
C            SOLUTION PHASE ACTIVITY COEFFICIENTS, (DIMENSIONLESS)
C
C RKJK0  = THE THERMODYNAMIC EXCHANGE CONSTANT, KJK (DIMENSIONLESS)
C
C RKKI   = THE KVJK VANSELOW SELECTIVITY COEFFICIENT ADJUSTED TO
C INCORPORATE
C            SOLUTION PHASE ACTIVITY COEFFICIENTS, (DIMENSIONLESS)
C
C RKKI0  = THE THERMODYNAMIC EXCHANGE CONSTANT, KKI (DIMENSIONLESS)
C
C SNPFRC = PROPROTION OF THE TOTAL CATIONIC CHARGE FOUND IN THE SOLUTION
C            PHASE (DIMENSIONLESS)
C
C TABLE  = ARRAY OF SOLUTION PHASE COMPOSITI0NS (DIMENSIONLESS)
C
C TFRACI = PROPROTION OF THE TOTAL SYSTEM CATIONIC CHARGE
C            BORN BY THE I IONS (DIMENSIONLESS)
C
C TFRACJ = PROPROTION OF THE TOTAL SYSTEM CATIONIC CHARGE
C            BORN BY THE J IONS (DIMENSIONLESS)
C
C TFRACK = PROPROTION OF THE TOTAL SYSTEM CATIONIC CHARGE
C            BORN BY THE K IONS (DIMENSIONLESS)
C
C THETA  = THE VOLUMETRIC WATER CONTENT(DECIMETER^3/DECIMETER^3)
C
C TOL    = ITERATIVE TOLERENCE FOR ROOT MEAN SQUARE ERROR
C            OF THE EXCHANGER PHASE ESTIMATES
C
C DENOM =   THE DENOMINATOR IN THE REFERENCE FUNCTION FOR EXCHANGER PHASE
C            ACTIVITY (UNITS VARY E.G. VANSELOW:MOL/KG, GAINES-THOMAS:
C            MOL(+)/KG)
C
C ZI     = THE VALENCE OF ION I (DIMENSIONLESS)
C
C ZJ     = THE VALENCE OF ION J (DIMENSIONLESS)
C
C ZK     = THE VALENCE OF ION K (DIMENSIONLESS)
C
```

```
C
C MAIN PROGRAM
C
C N     = THE DIMENSION OF THE TABLE TO BE WRITTEN TO ARRAY "TABLE"
C
C RN    = RATIONAL VALUE OF THE INTEGER VARIABLE "N"
C
C I     = OUTER DO LOOP VARIABLE
C
C ILOWER = DEBUGGING AID. SUBROUTINE BLCKBX WILL NOT BE CALLED IF THE
C          LOOP VARIABLE I IS LESS THAN THIS VARIABLE
C
C IUPPER = DEBUGGING AID. SUBROUTINE BLCKBX WILL NOT BE CALLED IF THE
C          LOOP VARIABLE I IS LESS THAN THIS VARIABLE
C
C J     = INNER DO LOOP VARIABLE
C
C JLOWER = DEBUGGING AID. SUBROUTINE BLCKBX WILL NOT BE CALLED IF THE
C          LOOP VARIABLE J IS LESS THAN THIS VARIABLE
C
C JUPPER = DEBUGGING AID. SUBROUTINE BLCKBX WILL NOT BE CALLED IF THE
C          LOOP VARIABLE I IS GREATER THAN THIS VARIABLE
C
C NJ    = N MINUS J, USED IN CONSTRUCTION OF UPPER DIAGONAL OF "TABLE"
C
C
C SUBROUTINE BLCKBX AND THE ATHENB SUBROUTINES
C
C
C
C ITER1 = THE COUNTER FOR THE INNER ITERATIVE LOOP
C
C ITER2 = THE COUNTER FOR THE OUTER ITERATIVE LOOP
C
C CBARI0 = HOLDS ORIGINAL VALUE OF CBARI DURING ITERATIVE SOLUTION
C
C CBARJ0 = HOLDS ORIGINAL VALUE OF CBARJ DURING ITERATIVE SOLUTION
C
C CBARK0 = HOLDS ORIGINAL VALUE OF CBARK  DURING ITERATIVE SOLUTION
C
C CBARI1 = HOLDS ORIGINAL VALUE OF CBARI DURING ITERATIVE SOLUTION
C
C CBARJ1 = HOLDS ORIGINAL VALUE OF CBARJ DURING ITERATIVE SOLUTION
C
C CBARK1 = HOLDS ORIGINAL VALUE OF CBARK DURING ITERATIVE SOLUTION
C
C CBARI2 = HOLDS ORIGINAL VALUE OF CBARI DURING ITERATIVE SOLUTION
C
C CBARJ2 = HOLDS ORIGINAL VALUE OF CBARJ DURING ITERATIVE SOLUTION
C
C CBARK2 = HOLDS ORIGINAL VALUE OF CBARK DURING ITERATIVE SOLUTION
C
C CBICI = VARIABLE USED IN THE ATHENB GROUP OF SUBROUTINES TO
C          REPLACE A GROUP OF VARIABLES FROM BEING RECALCULATED
C          REPEATEDLY
C
C CI0   = HOLDS ORIGINAL VALUE OF CI DURING ITERATIVE SOLUTION
C
```

```
C CJ0    = HOLDS ORIGINAL VALUE OF CJ DURING ITERATIVE SOLUTION
C
C CK0    = HOLDS ORIGINAL VALUE OF CK DURING ITERATIVE SOLUTION
C
C OSCTST = VARIABLE USED TO TEST FOR OSCILATORY SOLUTION
C
C RMSE   = CALCULATED ROOT MEAN SQUARE ERROR
C
C RMSE1  = RMSE VALUE OF PREVIOUS ITERATION, USED TO CHECK AGAINST
C          CONVERGENCE FAILURE DUE TO OSCILATORY SOLUTIONS
C
C
C
C SUBROUTINE OUTPUT
C
C
C CT     = TOTAL NORMALITY, RECALCULATED AS A CHECK
C
C CEC    = CATION EXCHANGE CAPACITY, RECALCULATED AS A CHECK
C
      CALL INPUT
      WRITE(4,140)TITLE
      IDEBUG  = 0
      IUPPER  = 100
      ILOWER  = -1
      JUPPER  = 100
      JLOWER  = -1
      CCTN = THETA*CTOTAL + BULKD*CECFIX
      EXPFRC = BULKD*CECFIX/CCTN
      SNPFRC = THETA*CTOTAL/CCTN
      N = MAXTAB
      RN = N
      DO 10 I = 0, N
         DO 9 J = 0,N
         IF(I.LT.ILOWER) GO TO 9
         IF(I.GT.IUPPER) GO TO 9
         IF(J.LT.JLOWER) GO TO 9
         IF(J.GT.JUPPER) GO TO 9
            NJ = N-J
            IF(I+J -N)2,2,9
    2       CONTINUE
               TFRACJ = I/RN
                  TFRACK = J/RN
                  TFRACI = 1.0 - TFRACJ - TFRACK
                  CALL CCALC
                  CALL BLCKBX(I,J)
                  CALL FCALC
                   IF(NJ-I) 3, 4, 3
    3          CONTINUE
                  TABLE(1,NJ,I) = EPFRCK
                  TABLE(1,I,NJ) = EPFRCJ
               GO TO 9
    4          CONTINUE
                  TABLE(1,I,NJ) = EPFRCJ
    9       CONTINUE
   10    CONTINUE
         DO 11 I = 0, N
         IF(IDEBUG.LT.1)WRITE(4,130) (TABLE(1,I,J),J=0,N)
```

```
   11 CONTINUE
  100 FORMAT(7X,12(8X,I3,10X))
  110 FORMAT(2X,I2,2X,12(1X,F2.0,F5.2,F5.2,F5.2,3X))
  120 FORMAT(12X,'NA',3X,'CA',3X,'MG',2(9X,'NA',3X,'CA',3X,'MG'))
  130 FORMAT(10G12.5)
  140 FORMAT(A)
      STOP
      END
C
C
C    ********************************************************************
C
C
C
      SUBROUTINE BLCKBX(III,JJJ)
C
C
C    ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK, MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK

    1 CONTINUE
      ITER1 = 0
      ITER2 = 0
      CBARI0 = CBARI
      CBARJ0 = CBARJ
      CBARK0 = CBARK
    5 CONTINUE
      CBARI1 = CBARI
      CBARJ1 = CBARJ
      CBARK1 = CBARK
      IJ = 0
      JK = 0
      KI = 0
      IJK = 0
   10 CONTINUE
          IF(IJ.GE.1) GO TO 20
            IF(CCI.LE.0.000001) GO TO 20
              IF(CCJ.LE.0.000001) GO TO 20
                CALL F
                CALL GAMMA
                CALL KCALC
                CALL ITHENJ
              IF(IJ.GE.1) GO TO 20
                CALL JTHENI
              IF(IJ.GE.1) GO TO 20
              GO TO 30
   20         CONTINUE
            IF(IJK.GE.2) GO TO 90
```

```
  30              CONTINUE
             IF(JK.GE.1) GO TO 40
                IF(CCJ.LE.0.000001) GO TO 40
                IF(CCK.LE.0.000001) GO TO 40
                    CALL F
                    CALL GAMMA
                    CALL KCALC
                    CALL JTHENK
             IF(JK.GE.1) GO TO 40
                CALL KTHENJ
             IF(JK.GE.1) GO TO 40
             GO TO 50
  40              CONTINUE
             IF(IJK.GE.2) GO TO 90
  50              CONTINUE
             IF(KI.EQ.1) GO TO 60
                IF(CCK.LE.0.000001) GO TO 60
                IF(CCI.LE.0.000001) GO TO 60
                    CALL F
                    CALL GAMMA
                    CALL KCALC
                    CALL KTHENI
                IF(KI.EQ.1) GO TO 60
                    CALL ITHENK
  60              CONTINUE
         IF(IJK-1) 100, 70, 90
  70   CONTINUE
          IF(CCI.LE.0.000001) GO TO 130
          IF(CCJ.LE.0.000001) GO TO 130
          IF(CCK.LE.0.000001) GO TO 130
          IF(ITER2.GE.ITRLIM) GO TO 110
              ITER2 = ITER2 + 1
              GO TO 10
  90   CONTINUE
       ITER2 = 0
       RMSE = DSQRT(((CBARI - CBARI1)**2 + (CBARJ - CBARJ1)**2)
      & + (CBARK - CBARK1)**2)/3.0
       IF(RMSE.LE.TOL) GO TO 130
C        IF(ITER1.GE.980)
C     &WRITE(4,*)III,JJJ,' CBARI ', CBARI, CBARJ, CBARK
       IF(ITER1.GE.ITRLIM) GO TO 120
       ITER1 = ITER1 + 1
       GO TO 5
 100   CONTINUE
          IF(CCI.LE.0.000001.AND.CCJ.LE.0.000001) GO TO 130
          IF(CCI.LE.0.000001.AND.CCK.LE.0.000001) GO TO 130
          IF(CCJ.LE.0.000001.AND.CCK.LE.0.000001) GO TO 130
          IF(IDEBUG.GE.1)WRITE(4,*) CCI, CCJ, CCK
          IF(IDEBUG.GE.1)WRITE(4,*) CI, CJ, CK
          IF(IDEBUG.GE.1)WRITE(4,*) CBARI,CBARJ, CBARK
          WRITE(4,*)III, JJJ,'  NONE OF THE SIX SUBROUTINES CONVERGED'
       GO TO 140
 110   CONTINUE
       WRITE(4,*)'STABLE FIRST ESTIMATE NOT ACHIEVED'
       WRITE(4,*)III,JJJ,'AFTER', ITER2,' ITERATIONS'
       GO TO 140
 120   CONTINUE
       WRITE(4,*) 'STABLE FINAL ESTIMATE NOT ACHIEVED'
```

```
      WRITE(4,*) III, JJJ,' AFTER', ITER2,' ITERATIONS'
      GO TO 140
130   CONTINUE
140   CONTINUE
150   CONTINUE
      RETURN
      END

C
C
C     ********************************************************************
C
C
C
      SUBROUTINE CCALC
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CCI = (CCTN*TFRACI)/ZI
      CCJ = (CCTN*TFRACJ)/ZJ
      CCK = (CCTN*TFRACK)/ZK
      CI = CCI*SNPFRC/THETA
      CJ = CCJ*SNPFRC/THETA
      CK = CCK*SNPFRC/THETA
      CBARI = CCI*EXPFRC/BULKD
      CBARJ = CCJ*EXPFRC/BULKD
      CBARK = CCK*EXPFRC/BULKD
      CALL DNMNTR
      RETURN
      END

C
C
C     ********************************************************************
C
C
C
      SUBROUTINE DNMNTR
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
```

```
      &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
      &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
      &ISBMKR, ITRLIM, JK,   MAXTAB, RKIJ, RKIJO, RKJK,
      &RKJKO, RKKI, RKKIO, SNPFRC, TABLE (4,0:101,0:101),
      &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK

      IF(IRF-2) 1,3,2
    1 CONTINUE
      DENOM = CBARI + CBARJ + CBARK
      GO TO 7
    2 CONTINUE
      DENOM = ((ZI + 1.0)*CBARI + (ZJ + 1.0)*CBARJ +
     &         (ZK + 1.0)*CBAARK)/2.0
      GO TO 7
    3 CONTINUE
      CEC = ZI*CBARI + ZJ*CBARJ + ZK*CBARK
      IF(ISBMKR.EQ.1) GO TO 4
      IF(ISBMKR.EQ.2) GO TO 6
      IF(ISBMKR.EQ.3) GO TO 4
      IF(ISBMKR.EQ.4) GO TO 5
      IF(ISBMKR.EQ.5) GO TO 6
      IF(ISBMKR.EQ.6) GO TO 5
    4 CONTINUE
      DENOM = CEC*((ZJ**ZI)*(ZI**(-ZJ)))**(1.0/(ZJ-ZI))
      GO TO 7
    5 CONTINUE
      DENOM = CEC*((ZK**ZJ)*(ZJ**(-ZK)))**(1.0/(ZK-ZJ))
      GO TO 7
    6 CONTINUE
      DENOM = CEC*((ZI**ZK)*(ZK**(-ZI)))**(1.0/(ZI-ZK))
      GO TO 7
    7 CONTINUE
      RETURN
      END

C
C
C
C     *********************************************************************
C
C
C
      SUBROUTINE F
C
C
C     *********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
      &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
      &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
      &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
      &ISBMKR, ITRLIM, JK,   MAXTAB, RKIJ, RKIJO, RKJK,
      &RKJKO, RKKI, RKKIO, SNPFRC, TABLE (4,0:101,0:101),
      &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK

      FI = 1.0
```

```
      FJ = 1.0
      FK = 1.0
      RETURN
      END
C
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE FCALC
C
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKIO, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      TEQUIV = ZI*CBARI + ZJ*CBARJ + ZK*CBARK
      EPFRCI = (ZI*CBARI)/TEQUIV
      EPFRCJ = (ZJ*CBARJ)/TEQUIV
      EPFRCK = (ZK*CBARJ)/TEQUIV
      RETURN
      END
C
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE GAMMA
C
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKIO, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK

      IF(IDAVIS) 10,10,5
    5 CONTINUE
      ZISQR = ZI**2.0
      ZJSQR = ZJ**2.0
      ZKSQR = ZK**2.0
```

```
      SI = (CI*ZISQR + CJ*ZJSQR + CK*ZKSQR)/2.0
      RTSI = DSQRT(SI)
      DVSBSS = - ((RTSI/(1.0 + RTSI))-0.2*SI)/2.0
      GAMMAI = DEXP(ZISQR*DVSBSS)
      GAMMAJ = DEXP(ZJSQR*DVSBSS)
      GAMMAK = DEXP(ZKSQR*DVSBSS)
  10  CONTINUE
      GAMMAI = 1.0
      GAMMAJ = 1.0
      GAMMAK = 1.0
      RETURN
      END


C
C
C
C     ***********************************************************************
C
C
C
      SUBROUTINE INPUT
C
C
C     ***********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK, IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      READ(10,1000) TITLE
      READ(10,1010) BULKD
      READ(10,1010) CECFIX
      READ(10,1010) CTOTAL
      READ(10,1010) THETA
      READ(10,1010) ZI
      READ(10,1010) ZJ
      READ(10,1010) ZK
      READ(10,1010) RKIJ0
      READ(10,1010) RKJK0
      READ(10,1010) RKKI0
      READ(10,1010) TOL
      READ(10,1020) ITRLIM
      READ(10,1020) MAXTAB
      READ(10,1020) IRF
      READ(10,1020) IDAVIS
      READ(10,1020) IDEBUG
      WRITE(*,1000) TITLE
      WRITE(*,1010) BULKD
      WRITE(*,1010) CECFIX
      WRITE(*,1010) CTOTAL
      WRITE(*,1010) THETA
      WRITE(*,1010) ZI
```

```
      WRITE(*,1010) ZJ
      WRITE(*,1010) ZK
      WRITE(*,1010) RKIJ0
      WRITE(*,1010) RKJK0
      WRITE(*,1010) RKKI0
      WRITE(*,1010) TOL
      WRITE(*,1020) ITRLIM
      WRITE(*,1020) MAXTAB
      WRITE(*,1020) IRF
      WRITE(*,1020) IDAVIS
      WRITE(*,1020) IDEBUG
 1000 FORMAT(A)
 1010 FORMAT(G15.7)
 1020 FORMAT(I10)
 1030 FORMAT(7X,A)
      RETURN
      END
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE ITHENJ
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CBARI0 = CBARI
      CBARJ0 = CBARJ
      CBARI1 = CBARI
      CBARJ1 = CBARJ
      CI0 = CI
      CJ0 = CJ
      ITER = 0
      RMSE = 0.01
 10   CONTINUE
      ITER = ITER + 1
      RMSE1 = RMSE
      CBARI2 = CBARI1
      CBARJ2 = CBARJ1
      CBARI1 = CBARI
      CBARJ1 = CBARJ
      CBICI = ((((CBARJ/CJ)**ZI)*(DENOM**(ZJ-ZI)))/RKIJ)**(1.0/ZJ)
      CI = CCI/(BULKD*CBICI) + THETA)
      CBARI = CCI/((THETA/CBICI) + BULKD)
      CJ = (CTOTAL - ZI*CI - ZK*CK)/ZJ
      CBARJ = (CECFIX - ZI*CBARI - ZK*CBARK)/ZJ
```

```
        IF(IDEBUG.GE.1) WRITE(4,*)'ITHENJ'
        IF(IDEBUG.GE.1) WRITE(4,*) ITER
        IF(IDEBUG.GE.1) WRITE(4,*)'CI, CJ, CK  ',CI, CJ, CK
        IF(IDEBUG.GE.1) WRITE(4,*)'CBARI, CBARJ, CBARK ',CBARI, CBARJ,
     CBARK
        CALL DNMNTR
        IF(CJ) 60, 60, 20
   20        CONTINUE
         IF(CBARJ) 60, 60, 30
   30        CONTINUE
        RMSE = DSQRT(((CBARI - CBARI1)**2 + (CBARJ - CBARJ1)**2)/2)
        IF(RMSE - TOL) 50, 50, 40
   40        CONTINUE
         IF(ITER-2) 49, 41, 41
   41        CONTINUE
             OSCTST = DSQRT(((CBARI-CBARI2)**2 + (CBARJ-CBARJ2)**2)/2)
             IF(OSCTST - TOL) 43,43,42
   42          CONTINUE
        IF(RMSE1-RMSE) 43,49,49
   43              CONTINUE
                CBARJ = (CBARJ + CBARJ1)/2
                CJ = (CCJ-(CBARJ*BULKD))/THETA
                CBARI = (CECFIX - ZJ*CBARJ - ZK*CBARK)/ZI
                CI =(CTOTAL - ZJ*CJ - ZK*CK)/ZI
                RMSE = 0.01
   49        CONTINUE
         IF(ITRLIM - ITER) 60, 10, 10
   50        CONTINUE
         IJ = 1
        GO TO 70
   60        CONTINUE
         CI = CI0
        CJ = CJ0
        CBARI = CBARI0
        CBARJ = CBARJ0
        CALL DNMNTR
   70        CONTINUE
         IJK = IJ + JK + KI
        RETURN
        END
C
C
C
C   ******************************************************************
C
C
C
        SUBROUTINE ITHENK
C
C
C   ******************************************************************
C
C
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
```

```
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CBARI0 = CBARI
      CBARK0 = CBARK
      CBARI1 = CBARI
      CBARK1 = CBARK
      CI0 = CI
      CK0 = CK
      ITER = 0
      RMSE = 0.01
10    CONTINUE
      ITER = ITER + 1
      RMSE1 =RMSE
      CBARI2 = CBARI1
      CBARK2 = CBARK1
      CBARI1 = CBARI
      CBARK1 = CBARK
      CBICI = (RKKI*((CBARK/CK)**ZI)*(DENOM**(ZK-ZI)))**(1.0/ZK)
      CI = CCI/(BULKD*CBICI + THETA)
      CBARI = CCI/((THETA/CBICI) + BULKD)
      CK = (CTOTAL - ZI*CI - ZJ*CJ)/ZK
      CBARK = (CECFIX - ZI*CBARI - ZJ*CBARJ)/ZK
      CALL DNMNTR
      IF(IDEBUG.GE.1)WRITE(4,*) 'ITHENK'
      IF(IDEBUG.GE.1)WRITE(4,*) ITER
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK  ',CI, CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',CBARI,
     &CBARJ, CBARK
      IF(CK) 60, 60, 20
20       CONTINUE
        IF(CBARK) 60, 60, 30
30       CONTINUE
      RMSE = DSQRT(((CBARI - CBARI1)**2 + (CBARK - CBARK1)**2)/2)
      IF(RMSE - TOL) 50, 50, 40
40       CONTINUE
        IF(ITER-2) 49, 41, 41
41       CONTINUE
        OSCTST = DSQRT(((CBARI-CBARI2)**2 + (CBARK-CBARK2)**2)/2)
          IF(OSCTST - TOL) 43,43,42
42         CONTINUE
      IF(RMSE1-RMSE) 43,49,49
43           CONTINUE
             CBARK = (CBARK + CBARK1)/2
             CK = (CCK-(CBARK*BULKD))/THETA
             CBARI = (CECFIX - ZJ*CBARJ - ZK*CBARK)/ZI
             CI =(CTOTAL - ZJ*CJ - ZK*CK)/ZI
             RMSE = 0.01
49       CONTINUE
        IF(ITRLIM - ITER) 60, 10, 10
50       CONTINUE
      KI = 1
    GO TO 70
60       CONTINUE
      CI = CI0
    CK = CK0
    CBARI = CBARI0
    CBARK = CBARK0
```

```
      CALL DNMNTR
   70      CONTINUE
         IJK = IJ + JK + KI
      RETURN
      END
C
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE JTHENI
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJO, RKJK,
     &RKJKO, RKKI, RKKIO, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CBARI0 = CBARI
      CBARJ0 = CBARJ
      CBARI1 = CBARI
      CBARJ1 = CBARJ
      CI0 = CI
      CJ0 = CJ
      ITER = 0
      RMSE = 0.01
   10 CONTINUE
      ITER = ITER + 1
      RMSE1 = RMSE
      CBARI2 = CBARI1
      CBARJ2 = CBARJ1
      CBARI1 = CBARI
      CBARJ1 = CBARJ
      CBJCJ = (RKIJ*((CBARI/CI)**ZJ)*((DENOM)**(ZI-ZJ)))**(1.0/ZI)
      CJ = CCJ/(BULKD*CBJCJ + THETA)
      CBARJ = CCJ/((THETA/CBJCJ) + BULKD)
      CI = (CTOTAL - ZJ*CJ - ZK*CK)/ZI
      CBARI = (CECFIX - ZJ*CBARJ - ZK*CBARK)/ZI
      CALL DNMNTR
      IF(IDEBUG.GE.1)WRITE(4,*) 'JTHENI'
      IF(IDEBUG.GE.1)WRITE(4,*) ITER
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK  ',CI, CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',
     &CBARI, CBARJ, CBARK
      IF(CI) 60, 60, 20
   20      CONTINUE
        IF(CBARI) 60, 60, 30
   30      CONTINUE
      RMSE = DSQRT((((CBARI - CBARI1)**2 + (CBARJ - CBARJ1)**2)/2)
      IF(RMSE - TOL) 50, 50, 40
```

```
      40        CONTINUE
                IF(ITER-2) 49, 41, 41
      41        CONTINUE
                OSCTST = DSQRT(((CBARI-CBARJ2)**2 + (CBARJ-CBARJ2)**2)/2)
                  IF(OSCTST - TOL) 43,43,42
      42          CONTINUE
          IF(RMSE1-RMSE) 43,49,49
      43              CONTINUE
                      CBARI = (CBARI + CBARI1)/2
                      CI = (CCI-(CBARI*BULKD))/THETA
                      CBARJ = (CECFIX - ZI*CBARI - ZK*CBARK)/ZJ
                      CJ =(CTOTAL - ZI*CI - ZK*CK)/ZJ
                      RMSE = 0.01
      49        CONTINUE

            IF(ITRLIM - ITER) 60, 10, 10
      50        CONTINUE
              IJ = 1
          GO TO 70
      60        CONTINUE
            CI = CI0
          CJ = CJ0
          CBARI = CBARI0
          CBARJ = CBARJ0
          CALL DNMNTR
      70        CONTINUE
              IJK = IJ + JK + KI
          RETURN
          END
C
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE JTHENK
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CBARJ0 = CBARJ
      CBARK0 = CBARK
      CBARJ1 = CBARJ
      CBARK1 = CBARK
      CJ0 = CJ
      CK0 = CK
      ITER = 0
      RMSE = 0.01
```

```
10    CONTINUE
      ITER = ITER + 1
      RMSE1 = RMSE
      CBARJ2 = CBARJ1
      CBARK2 = CBARK1
      CBARJ1 = CBARJ
      CBJK1 = CBARK
      CBJCJ = ((((CBARK/CK)**ZJ)*((DENOM)
     &**(ZK-ZJ)))/RKJK)**(1.0/ZK)
      CJ = CCJ/(BULKD*CBJCJ + THETA)
      CBARJ = CCJ/((THETA/CBJCJ) + BULKD)
      CK = (CTOTAL - ZI*CI - ZJ*CJ)/ZK
      CBARK = (CECFIX - ZI*CBARI - ZJ*CBARJ)/ZK
      CALL DNMNTR
      RMSE = DSQRT(((CBARJ - CBARJ1)**2 + (CBARK - CBARK1)**2)/2)
      IF(IDEBUG.GE.1) WRITE(4,*) 'JTHENK'
      IF(IDEBUG.GE.1)WRITE(4,*) ITER
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK ',CI, CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',
     &CBARI, CBARJ, CBARK
      IF(CK) 60, 60, 20
20        CONTINUE
       IF(CBARK) 60, 60, 30
30        CONTINUE
      RMSE = DSQRT(((CBARJ - CBARJ1)**2 + (CBARK - CBARK1)**2)/2)
      IF(RMSE - TOL) 50, 50, 40
40        CONTINUE
          IF(ITER-2) 49, 41, 41
41        CONTINUE
          OSCTST = DSQRT(((CBARJ-CBARJ2)**2 + (CBARK-CBARK2)**2)/2)
            IF(OSCTST - TOL) 43,43,42
42          CONTINUE
      IF(RMSE1-RMSE) 43,49,49
43            CONTINUE
                CBARK = (CBARK + CBARK1)/2
                CK = (CCK-(CBARK*BULKD))/THETA
                CBARJ = (CECFIX - ZI*CBARI - ZK*CBARK)/ZJ
                CJ =(CTOTAL - ZI*CI - ZK*CK)/ZJ
                RMSE = 0.01
49        CONTINUE
       IF(ITRLIM - ITER) 60, 10, 10
50        CONTINUE
      JK = 1
      GO TO 70
60        CONTINUE
      CJ = CJ0
      CK = CK0
      CBARJ = CBARJ0
      CBARK = CBARK0
      CALL DNMNTR
70        CONTINUE
      IJK = IJ + JK + KI
      RETURN
      END

C
C
```

```
C     *********************************************************************
C
C
C
      SUBROUTINE KCALC
C
C
C     *********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK

      RKIJ = RKIJ0 * (( FI/GAMMAI )**ZJ ) *
     &(( GAMMAJ/FJ )**ZI )
      RKJK = RKJK0 * (( FJ/GAMMAJ )**ZK ) *
     &(( GAMMAK/FK )**ZJ )
      RKKI = RKKI0 * (( FK/GAMMAK )**ZI ) *
     &(( GAMMAI/FI )**ZK )
      RETURN
      END

C
C
C     *********************************************************************
C
C
C
      SUBROUTINE KTHENI
C
C
C     *********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
      CBARI0 = CBARI
      CBARK0 = CBARK
      CBARI1 = CBARI
      CBARI1 = CBARK
      CI0 = CI
      CK0 = CK
      ITER = 0
      RMSE = 0.01
```

```
10    CONTINUE
      RMSE1 = RMSE
      ITER = ITER + 1
      CBARI2 = CBARI1
      CBARK2 = CBARK1
      CBARI1 = CBARI
      CBARK1 = CBARK
      CALL DNMNTR
      CBKCK = ((((CBARI/CI)**ZK)*(DENOM**(ZI-ZK)))/RKKI)**(1.0/ZI)
      CK = CCK/(BULKD*CBKCK + THETA)
      CBARK = CCK/((THETA/CBKCK) + BULKD)
      CI = (CTOTAL - ZJ*CJ - ZK*CK)/ZI
      CBARI = (CECFIX - ZJ*CBARJ - ZK*CBARK)/ZI
      CALL DNMNTR
      IF(IDEBUG.GE.1)WRITE(4,*) 'KTHENI'
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK  ',CI,CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',
     &CBARI, CBARJ, CBARK
      IF(CI) 60, 60, 20
20    CONTINUE
      IF(CBARI) 60, 60, 30
30    CONTINUE
      RMSE = DSQRT(((CBARI - CBARI1)**2 + (CBARK - CBARK1)**2)/2)
      IF(IDEBUG.GE.1)WRITE(4,*) 'KTHENI',ITER,RMSE, RMSE1,CBARI
      IF(IDEBUG.GE.1)WRITE(4,*) ITER
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK  ',CI,CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',
     &CBARI, CBARJ, CBARK
      IF(RMSE - TOL) 50, 50, 40
40    CONTINUE
      IF(ITER-2) 49, 41, 41
41    CONTINUE
      OSCTST = DSQRT(((CBARI-CBARI2)**2 + (CBARK-CBARK2)**2)/2)
      IF(OSCTST - TOL) 43,43,42
42    CONTINUE
      IF(RMSE1-RMSE) 43,49,49
43    CONTINUE
      CBARI = (CBARI + CBARI1)/2
      CI = (CCI-(CBARI*BULKD))/THETA
      CBARK = (CECFIX - ZI*CBARI - ZJ*CBARJ)/ZK
      CK =(CTOTAL - ZI*CI - ZJ*CJ)/ZK
      RMSE = 0.01
49    CONTINUE
      IF(ITRLIM - ITER) 60, 10, 10
50    CONTINUE
      KI = 1
      GO TO 70
60    CONTINUE
      CI = CI0
      CK = CK0
      CBARI = CBARI0
      CBARK = CBARK0
      CALL DNMNTR
70    CONTINUE
      IJK = IJ + JK + KI
      RETURN
      END
```

```
C
C
C     ********************************************************************
C
C
C
      SUBROUTINE KTHENJ
C
C
C     ********************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
             CBARI0 = CBARI
      CBARJ0 = CBARJ
      CBARK0 = CBARK
      CBARJ1 = CBARJ
      CBARK1 = CBARK
      CJ0 = CJ
      CK0 = CK
      ITER = 0
      RMSE = 0.01
10    CONTINUE
      ITER = ITER + 1
      RMSE1 = RMSE
      CBARJ2 = CBARJ1
      CBARK2 = CBARK1
      CBARJ1 = CBARJ
      CBARK1 = CBARK
      CBKCK = (RKJK*((CBARJ/CJ)**ZK)*(DENOM**(ZJ-ZK)))**(1.0/ZJ)
      CK = CCK/(BULKD*CBKCK + THETA)
      CBARK = CCK/((THETA/CBKCK) + BULKD)
      CJ = (CTOTAL - ZI*CI - ZK*CK)/ZJ
      CBARJ = (CECFIX - ZI*CBARI - ZK*CBARK)/ZJ
      CALL DNMNTR
      RMSE = DSQRT(((CBARJ - CBARJ1)**2 + (CBARK - CBARK1)**2)/2)
      IF(IDEBUG.GE.1)WRITE(4,*) 'KTHENJ'
      IF(IDEBUG.GE.1)WRITE(4,*) ITER
      IF(IDEBUG.GE.1)WRITE(4,*)'CI, CJ, CK  ',CI, CJ, CK
      IF(IDEBUG.GE.1)WRITE(4,*)'CBARI, CBARJ, CBARK ',
     &CBARI, CBARJ, CBARK
      IF(CJ) 60, 60, 20
20       CONTINUE
      IF(CBARJ) 60, 60, 30
30       CONTINUE
      RMSE = DSQRT(((CBARJ - CBARJ1)**2 + (CBARK - CBARK1)**2)/2)
      IF(RMSE - TOL) 50, 50, 40
40       CONTINUE
         IF(ITER-2) 49, 41, 41
41       CONTINUE
```

```
           OSCTST = DSQRT((((CBARJ-CBARJ2)**2 + (CBARK-CBARK2)**2)/2)
              IF(OSCTST - TOL) 43,43,42
    42         CONTINUE
       IF(RMSE1-RMSE) 43,49,49
    43         CONTINUE
               CBARJ = (CBARJ + CBARJ1)/2
               CJ = (CCJ-(CBARJ*BULKD))/THETA
               CBARK = (CECFIX - ZI*CBARI - ZJ*CBARJ)/ZK
               CK =(CTOTAL - ZI*CI - ZJ*CJ)/ZK
               RMSE = 0.01
    49         CONTINUE
       IF(ITRLIM - ITER) 60, 10, 10
    50         CONTINUE
               JK = 1
       GO TO 70
    60         CONTINUE
          CJ = CJO
       CK = CKO
       CBARJ = CBARJO
       CBARK = CBARKO
       CALL DNMNTR
    70         CONTINUE
          IJK = IJ + JK + KI
       RETURN
       END
C
C
C
C     ****************************************************************
C
C
C
C
       SUBROUTINE KWRITE
C
C
C
C     ****************************************************************
C
C
C
C
C
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
      &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
      &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
      &GAMMAI, GAMMAJ, GAMMAK,IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
      &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJO, RKJK,
      &RKJKO, RKKI, RKKIO, SNPFRC, TABLE(4,0:101,0:101),
      &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK
       TOT = CBARI + CBARJ + CBARK
       TN = ZI*CI + ZJ*CJ + ZK*CK
       CEC= ZI*CBARI + ZJ*CBARJ + ZK*CBARK
       CBARI = CBARI + 0.1d-14
       CBARJ = CBARJ + 0.1d-14
       CBARK = CBARK + 0.1d-14
       CI = CI + 0.1d-14
       CJ = CJ + 0.1d-14
       CK = CK + 0.1d-14
       RIJ = ((CI/CBARI)**ZJ)*((CBARJ/CJ)**ZI)*(TOT**(ZJ-ZI))
```

```
      RJK = ((CJ/CBARJ)**ZK)*((CBARK/CK)**ZJ)*(TOT**(ZK-ZJ))
      RKI = ((CK/CBARK)**ZI)*((CBARI/CI)**ZK)*(TOT**(ZI-ZK))
      WRITE(4,100)TFRACI, TFRACJ, TFRACK, RIJ, RJK, RKI
  100 FORMAT(1X,6F12.5)
      RETURN
      END



C
C
C   ******************************************************************
C
C
C
      SUBROUTINE OUTPUT
C
C
C   ******************************************************************
C
C
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/STEVES/BULKD, CBARI, CBARJ, CBARK, CCI, CCJ, CCK,
     &CCTN, CECFIX, CI, CJ, CK, CTOTAL, DENOM,
     &FI, FJ, FK, EPFRCI, EPFRCJ, EPFRCK, EXPFRC,
     &GAMMAI, GAMMAJ, GAMMAK, IDAVIS, IDEBUG, IJ, IJK, KI, IRF,
     &ISBMKR, ITRLIM, JK,  MAXTAB, RKIJ, RKIJ0, RKJK,
     &RKJK0, RKKI, RKKI0, SNPFRC, TABLE(4,0:101,0:101),
     &TFRACI, TFRACJ, TFRACK, THETA, TITLE, TOL, ZI, ZJ, ZK


      CT = ZI*CI + ZJ*CJ +ZK*CK
      CEC = ZI*CBARI + ZJ*CBARJ + ZK*CBARK
      CCI = THETA*CI + BULKD*CBARI
      CCJ = THETA*CJ + BULKD*CBARJ
      CCK = THETA*CK + BULKD*CBARK
      RETURN
      END
```

APPENDIX C

OPERATING PROGRAM BLCKBX

Program BLCKBX was written in FORTRAN 77 and implemented
on a Digital Equipment Corporation VAX 11/750 minicomputer.
To run the program, an input file with physical, chemical,
and computational parameters is written. Below is a listing
of an input file which would instruct Program BLCKBX to
created a 50x50x50 ternary exchange isotherm using the mole
fraction exchanger phase reference function.

```
MOLE FRACTION REFERENCE FUNCTION
 1.161239      : Bulk Density (kg/dec3)
 0.4494000E-02 : Cation Exchange Capacity (mol(+)/kg)
 0.1055000E-01 : Total Normality (mol(+)/dec3)
 0.2510000     : Moisture content (dec3/dec3)
 1.000000      : Valence for the 1st ion
 2.000000      : Valence for the 2nd ion
 2.000000      : Valence for the 3rd ion
 7.215056      : Thermodynamic exchange constant for KEX12
 0.4120000E-02 : Thermodynamic exchange constant for KEX23
 2.159399      : Thermodynamic exchange constant for KEX31
 0.1000000E-08 : Tolerance for root mean square error
 100000        : Iterative limit
     50        : Maximum index in table (0..x)
      1        : Exchange Phase Reference Function=Mole Fraction
      0        : Implement Davies Equation
      0        : Print Debugging Write Statements
```

When running the program interactively, the program must
first be compiled using the commands

```
$ FORTRAN BLKBOX <return>
$ LINK BLKBOX <return>
```

If the file BLKBX.EXE is maintained in the user's directory, the two lines above do not need to be repeated. Then the program is the begun by typing

$ RUN BLKBOX <return>

The program then requests

INPUT FILE NAME

The user then types

input file name <return>

The computer then inquires

OUTPUT FILE NAME

and the user designates his or her choice

output file name <return>

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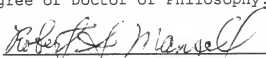
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BIOGRAPHICAL SKETCH

Steven Alexander Grant was born September 20, 1953, in Grand Rapids, Michigan. After graduating from Forest Hills High School in that city, he attended Michigan State University in East Lansing, receiving there his B.S. and M.S. in crop and soil sciences. Mr. Grant worked as an agricultural extensionist as a Peace Corps volunteer in Tunisia from 1981 through 1983. He has been a doctoral student at the University of Florida since leaving the Peace Corps. He is a member of American Society of Agronomy, Soil Science Society of America, International Society of Soil Science, Alpha Zeta, Gamma Sigma Delta, and an associate member of Sigma Xi.

I certify that I have read this study and that in my
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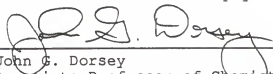a dissertation for the degree of Doctor of Philosophy.

Robert S. Mansell, Chairman
Professor of Soil Science

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R. Dean Rhue, Cochairman
Associate Professor of Soil Science

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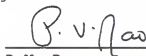a dissertation for the degree of Doctor of Philosophy.

John G. Dorsey
Associate Professor of Chemistry

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Clifford T. Johnston
Assistant Professor of Soil Science

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a dissertation for the degree of Doctor of Philosophy.

P.V. Rao
Professor of Statistics

This dissertation was submitted to the Graduate Faculty of
the College of Agriculture and to the Graduate School and was
accepted as partial fulfillment of the requirements for the
degree of Doctor of Philosophy.

December, 1987

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Dean, College of Agriculture

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